Environment Canada Environnement Canada

Guidelines for Surface Water Quality

Vol. 1 Inorganic Chemical Substances

ZINC

Margaret C. Taylor and Adrian Demayo

INLAND WATERS DIRECTORATE,
WATER QUALITY BRANCH,
OTTAWA, CANADA, 1983.

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Reviews on Purpose

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Abstract

A literature survey was carried out on the toxic effects qf zinc and zinc compounds on human health, aquatic life, plants and livestock. The information is summarized in this publication. From it, maximum zinc concentrations in water at which toxic effects will not appear are recommended.

Résumé

On a effectué une étude de la documentation portant sur les effets toxiques du zinc et de composés du zinc sur les humains, les organismes aquatiques, les plantes et le bétail. Ces données sont résumées dans cette publication. En se basant sur ces données, on propose des valeurs des concentrations maximales de zinc dans l'eau auxquelles on n'observe pas d'effets toxiques.

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RECOMMENDED WATER QUALITY OBJECTIVES FOR ZINC

Uses	Recommended objectives (as total zinc)
Raw public water supply	5 mg/L 10 mg/L for waters with pre-distribution treatment
Aquatic life and wildlife	0.05 mg/L, hardness 0-120 mg/L as $CaCO_3$ 0.10 mg/L, hardness 120-180 mg/L as $CaCO_3$ 0.20 mg/L, hardness 180-300 mg/L as $CaCO_3$ 0.30 mg/L, hardness >300 mg/L as $CaCO_3$
Agricultural water supply	
Livestock watering	50 mg/L
Irrigation	1 mg/L in soils with pH <6.5 5 mg/L in soils with pH >6.5
Recreation and aesthetics	5 mg/L
Industrial water supplies	
Food processing	5 mg/L 10 mg/L for waters with pre-distribution treatment

Guidelines for Surface Water Quality

Vol. 1. Inorganic Chemical Substances. Zinc

Margaret C. Taylor and Adrian Demayo

SOURCES, OCCURRENCE AND FORM

Natural Distribution of Zinc

The crustal (igneous rocks) average concentration of zinc has been estimated at 70 mg/kg, ranking it 24th among the elements found in the earth's crust (Taylor 1964; Bowen 1966, p. 16ff.). Other estimates of zinc concentrations in the earth's crust range from 5 to 200 mg/kg (Aylett 1973; Brooks 1977). Although better known, zinc is scarcer than less familiar elements such as zirconium or rubidium. The zinc concentration in sedimentary rocks has been estimated as follows: shales, 95 mg/kg; sandstones, 16 mg/kg; and limestones, 20 mg/kg. Deep-sea clay sediments contain an average of 165 mg/kg of zinc (Turekian and Wedepohl 1961).

Zinc is mainly found in British Columbia, the Silesia region of Poland, Burma, New South Wales (Australia) and in the United States (New Jersey and Missouri) as sulphide, carbonate, silicate and phosphate minerals. The main zinc ores are sphalerite (ZnS) and calamine or smithsonite ($ZnCO_3$ or $ZnCO_3+Zn_2SiO_4$) (Browning 1969; Aylett 1973). Manganese is often present in zinc minerals, contributing significantly to their colour (Farnsworth and Kline 1973).

In seawater the concentration of zinc has been estimated at 0.002 to 0.01 mg/L (Bowen 1966, pp. 19-20; Brooks 1977). Chester and Stoner (1974a) measured the zinc and other metal concentrations in some of the world's oceans and seas. The zinc concentrations ranged between 0.0006 and 0.0126 mg/L (average 0.0024 mg/L) in nearshore ocean surface waters (<400 km from land masses) and between 0.0003 and 0.003 mg/L (average 0.0014 mg/L) in open-ocean surface waters.

The zinc concentrations (as "extractable") in approximately 12 000 samples of river water collected in Canada between 1972 and 1977 ranged from less than 0.001 mg/L to approximately 3.0 mg/L. Ninety per cent of the results were less than 0.06 mg/L. There were several instances, especially from sampling points in the mining area of northeastern New Brunswick, in which the results were greater than 3.0 mg/L. The highest value found in these samples was 125 mg/L (Environment Canada 1977). For samples of lake water, the results were of the same order of magnitude. In almost 1400 samples they ranged from less than 0.001 mg/L to 1.0 mg/L. Ninety per cent of the results were less than 0.03 mg/L (Environment Canada 1977).

In a study conducted in the United States, zinc was detected in 76.5% of 1600 surface water samples collected between 1962 and 1967. The concentrations ranged from 0.002 to 1.183 mg/L with a mean of 0.064 mg/L (Kopp 1970). The mean zinc concentrations of groundwater samples from the non-mineral and mineral regions of Front Range, Colorado, were 0.2 and 0.31 mg/L, respectively (Klusman and Edwards 1977). The average zinc concentrations in the water of the Grand Calumet River system ranged between 0.057 and 0.080 mg/L, divided almost equally between filterable (0.45 μm membrane filter) and nonfilterable fractions. The average zinc concentrations in the sediments were between 750 and 2060 mg/kg (Romano *et al.* 1977).

High zinc concentrations were reported in water and sediment samples from rivers draining a mineralized region of England. The zinc concentrations in water samples ranged from 0.026 to 10.0 mg/L. In a river with a pH of 4 the range of zinc concentrations was from 1.52 to 10.0 mg/L. The zinc concentrations in a "control" river were between 0.011 and 0.049 mg/L. Similarly, the zinc concentrations in the sediments of rivers draining the mineralized areas ranged from 69 to 7000 mg/kg, whereas in the sediments of the control river they ranged from 31 to 370 mg/kg (Thornton and Webb 1975).

The zinc concentrations in sediments from the Miramichi and Restigouche Rivers of the metallogenic region of northeastern New Brunswick ranged from 48 to 104 mg/kg (air dry). The zinc concentrations in the sediments of the Nepisiguit River were much higher, from 82 to 520 mg/kg, reflecting the direct input of mining effluents into this river (Ray and White 1977).

Analysis of the sediments from the fresh water and estuarine sections of the Urr Water (a tributary of Solway Firth, United Kingdom), which is relatively unpolluted,

gave average zinc concentrations of 67.0 mg/kg (range, 43.0 to 97.5 mg/kg dry weight) and 41.2 mg/kg (range, 24.8 to 65.0 mg/kg), respectively (Taylor 1976).

The zinc concentrations in the top 4.45 cm of sediment from the Ottawa River were between 19 and 485 mg/kg with an average of 138 mg/kg. The zinc concentrations in sediments from the Rideau River (Ontario) were between 16 and 670 mg/kg with an average of 118 mg/kg (Oliver and Agemian 1974). Concentrations ranged from 2.5 to 393.5 mg/kg (to 865 mg/kg in Lake Michigan) in the sediments of tributaries to the Great Lakes (Hutchinson and Fitchko 1974). Sediments from Lake Superior (near Tofte, Minnesota) had concentrations from 80 to 160 mg/kg (Korda *et al.* 1977). The range of zinc concentrations in the top 1 or 2 cm of sediment samples from Lake Huron was 154 to 228 mg/kg; below a depth of 8 cm the range was 88 to 116 mg/kg. Similarly, the range in the top 1 cm of six sediment samples from Lake Erie was 192 to 419 mg/kg, while at greater depths it was 69 to 128 mg/kg. The top 1 cm of five sediment samples from Lake Ontario had a range of zinc concentrations from 319 to 600 mg/kg, while below 15 cm the range was 86 to 121 mg/kg (Kemp and Thomas 1976).

In a geochemical survey of the centre-lake sediments in the Province of Saskatchewan, it was found that although the range of zinc concentrations was wide (4 to 7100 mg/kg), 91% of the results lay within the much narrower range of 50 to 200 mg/kg (Garrett and Hornbrook 1976).

Production and Uses

In 1977 the estimated zinc mine production of the world was approximately 6 250 000 tonnes, of which 23% was produced in the Central Economy Countries and the rest in the Market Economy Countries. Canada produced 27% of the latter, followed by Peru and Australia with approximately 10% each. Zinc metal production in the Western World in 1977 amounted to 4 217 000 tonnes, and consumption was 4 284 000 tonnes (Brown 1978; U.S. Bureau of Mines 1978, pp. 190–191).

In Canada, zinc is produced together with lead, copper and silver. Approximately 38% of the zinc production comes from zinc ores, 13% from copper ores and the balance from mixed ores. Thirty per cent of the copper mine production, 100% of the lead mine production and 75% to 80% of silver production is produced jointly with zinc (Brown 1977a). Canada has the capacity to refine approximately 50% of its mine production, and in 1977 it operated at approximately 77% of this capacity. The average zinc content in ores is 5.3% and the average recovery is 84% (Brown 1978).

The domestic consumption of zinc in 1977 was approximately 125 000 tonnes, which represented only 9.6% of Canada's mine production or 2.9% of Western World consumption. Canada exports almost 90% of its production (34% as refined zinc and 55% as zinc ore). This amounts to 40% of all trade between major producing and consuming regions (Brown 1978).

About 35% of the total world production is used as zinc coatings to protect iron and steel by hot-dip galvanizing, electrogalvanizing, spraying, painting, or sherardizing. The other major use is in zinc alloys. Zinc is the major component—typically around 96% (the rest is aluminum and magnesium)—of alloys used in die casting. This use accounts for 25% of the world production of zinc. Another 20% of world zinc output is used in the production of brass, which can contain 5% to 45% zinc as well as copper and, sometimes, other metals (Aylett 1973; Browning 1969). Approximately 10% of the total production is used as zinc alone for producing rolled sheets and strips used in the manufacture of dry batteries, roofing and exterior fittings on buildings, and some printing processes (e.g., lithography).

In Canada, the percentages of zinc uses are somewhat different. Approximately 49% of zinc consumption in Canada is used for protective coatings, 20% in alloys for diecast parts, 11% in brass, and 20% for other uses which have zinc oxide as the major component (Brown 1978).

Pathways for Entering the Environment

Weathering of Zinc Minerals

Zinc is one of the elements which is easily mobilized by weathering (Brooks 1977). Ketchum (1975) computed a "Relative Critical Index" by dividing the estimated total (natural plus anthropogenic) input to the environment of a number of metals by the concentration considered to pose minimal risk of deleterious effect. Mainly because of its high rate of mobilization, zinc was ranked immediately after nickel and mercury, but before other well known toxic metals such as lead, arsenic and cadmium.

The approximate amount of zinc that enters the environment as a result of weathering phenomena can be calculated from the weathering rates of various types of rocks and their average zinc concentrations. The results, shown in Table 1, indicate that approximately 725 000 tonnes of zinc enters the environment through natural weathering processes. A similar value, 720 000 tonnes, was given by Bertine and Goldberg (1971). Bowen (1977) estimated that 370 000 tonnes of zinc is carried annually down to the sea by rivers. Of this amount, about 70% is removed by sediments.

Table 1. Estimated Zinc Input into the Environment as a Result of Weathering

Type of rock	Weathering rate,[1] million tonnes/year	Average zinc concentration,[2,3] mg/kg	Total zinc input to the environment, 000's tonnes/year
Igneous	700–1500	70	49–105
Shale	6500	95	618
Sandstone	1500	16	24
Limestone	300	20	6
TOTAL			697–753

[1] Eriksson 1960
[2] Turekian and Wedepohl 1961
[3] Taylor 1964

In a laboratory experiment zinc was extracted at a rate of 0.020 and 0.050 mg/day when gram quantities of sphalerite (ZnS) and smithsonite ($ZnCO_3$) were put in contact with circulating deionized water equilibrated with atmospheric CO_2. When the same minerals were in contact with a 0.1% humic acid solution of pH 3.4, the extraction rates were greater, 0.120 and 70 mg/day, respectively. For comparison, when the zinc metal was left in contact with water or with the humic acid solution, 0.160 and 37 mg, respectively, of the metal were extracted in 24 h (Baker 1973).

The zinc concentration in a stream flowing over a sulphide mineral bearing zone in the eastern United States was 0.03 mg/L and the pH, 6.5. The zinc concentration in the pyrite ore was 90 mg/kg. The concentration in the tailing pond and in the stream below was 1.06 mg/L, and the pH was 5.1 to 5.2. The silt (particle size, 105 to 5 μm) and the mud (5 to 0.2 μm) in the pond had zinc concentrations of 60 and 82 mg/kg, respectively (Schrader and Furbish 1978).

The annual worldwide emission of zinc to the atmosphere from soil erosion has been estimated at 25 000 tonnes. Other natural sources, i.e. forest fires, volcanos, vegetation and sea salt sprays, have been estimated to contribute an additional 18 500 tonnes to the annual zinc emissions (Nriagu 1979).

Table 2 summarizes the available data on natural and anthropogenic sources of zinc to the environment.

Anthropogenic Sources of Zinc to the Environment

Chester and Stoner (1974b) collected samples of the particulate matter at approximately 15 m above some of the world's oceans and found zinc concentrations of 135 to 3100 mg/kg, which represented an enrichment factor of 2.4 to 87 (average 13) over the crustal abundance. The authors concluded that this enrichment was due to anthropogenic sources. Similarly, Duce *et al.* (1975) found an enrichment factor over the crustal abundance of around 100 in a series of atmospheric particulate samples collected north of the 30°N parallel over the Atlantic Ocean and in tropospheric samples collected at the geographic South Pole (90°S, 2800 m above sea level). A more recent publication casts some doubts on these conclusions. Boutron and Lorius (1979) have found enrichment factors of approximately 10 to 65 for zinc in the Antarctic snow over the crustal abundance of zinc going back to 1914. They concluded that the high zinc enrichment factor was linked with natural phenomena, e.g., volcanism, rather than with global pollution. The measured zinc concentrations in the Antarctic snow ranged from 26 to 74 ng/kg.

Table 2. Estimated Annual Zinc Input to the Environment from Natural and Anthropogenic Sources

Source	Amount, thousand tonnes
Natural	
Weathering (see Table 1)	725
Erosion	25
Other	18.5
Total	768.5
Anthropogenic	
Primary zinc production	99
Wood combustion	75
Waste incineration	37
Iron and steel production	35
Other atmospheric emissions	68
Municipal wastewater	100
Total	414

References: Nriagu 1979; Galloway 1979.

There are several anthropogenic sources of zinc to the environment. The analysis of water from various dated strata of a permanent ice sheet in south Greenland showed that the zinc (also Cu and Cd; but not Hg, Sb, or As) concentrations were greater in the last 30 years than in the period before. The average zinc concentration for the samples dated 1807 to 1915 was 375 ng/kg, while the average of the samples dated 1966 to 1971 was 1047 ng/kg (Weiss *et al.* 1975). This increase was attributed to the so-called "cultural" factor, i.e., anthropogenic input. Similarly, in an inventory of several metals discharged into Chesapeake Bay, Helz (1976) concluded that at least 29% of the zinc input was of anthropogenic origin. The total zinc input to the bay was estimated at 2060 tonnes/year. Förstner (1977) estimated that around 90% of the zinc content of a representative sediment sample from the Lower Rhine was of civilizational origin. For comparison, 100% of the iron concentration was considered to be of natural origin.

Published data on the concentrations of various metals in sediments from various lakes in Europe and North

America were analyzed by Förstner (1976). For zinc, the background values (pre-industrial era) ranged from 7 mg/L in Lake Erie to 129 mg/L in Lake Michigan. Taking the ratio of the maximum zinc concentrations found in each of the lakes and the respective background value, Förstner calculated enrichment factors of 2.5 (Lake Michigan) to 6 (Lake Erie and Lake Monona). The author concluded that this enrichment was due mainly to public sewage systems. Similarly, Walters *et al.* (1974) reported sediment enrichment factors of 1.7 to 25 (average 7.6) for zinc in Lake Erie, with the highest values probably being caused by pollution inputs controlled by the "cultural" factor in the Detroit, Cleveland and Buffalo areas. The present-day zinc input to Lake Erie was calculated at 7.8 tonnes/year or between 21 and 510 mg/m^2.a depending on the location. The natural flux has been estimated at 7 to 148 mg/m^2.a, while the anthropogenic input was 10 to 362 mg/m^2.a. In percentage terms, the anthropogenic input at various sampling points ranged from 52% to 84% of the total input. Sixty-seven per cent of the input to the lake was calculated as being via the Detroit River; 57% of the total input was exported via the Niagara River and Welland Canal, the rest being retained in the sediments (Nriagu *et al.* 1979). The observed total zinc input to Lake Michigan was approximately 2630 tonnes/year of which almost 75% was retained in the sediment (Klein 1975). By analyzing a dated sediment core from an oxic fjord basin in Ranafjord in Northern Norway, Skei and Paus (1979) concluded that the influx of zinc has doubled during this century and that at the present time the anthropogenic input equals natural input. The natural flux of zinc to the sediments was estimated at approximately 135 mg/m^2.a, and in other basins of the Baltic Sea it was estimated at 70 mg/m^2.a.

Anthropogenic Zinc Emissions to the Atmosphere

Probably the most important anthropogenic sources of zinc are air emissions. A study of the metal's input to Lake Michigan showed that the mean daily dissolved zinc tributary input to Lake Michigan was approximately 500 kg/day. The atmospheric emissions of zinc from pollution sources in Chicago, Milwaukee and northwest Indiana were estimated at 11 000 kg/day of which probably at least 20% or 2200 kg/day entered the lake. Zinc, together with iron, manganese and copper, was the metal for which the potential atmospheric input was much larger than the tributary input (Robbins *et al.* 1972). Sixty-eight per cent of the current zinc input to Lake Washington sediments was estimated as being of aerial origin (Barnes and Schell 1973). From the available data it was calculated that almost 90% of the zinc input to Lake Michigan was via aerosol deposition and the remainder was via mobilization of soil (Klein 1975). The atmospheric input accounted for approximately 12% of the zinc input to Lake Erie (Nriagu *et al.* 1979).

Schell and Nevissi (1977) quoted data which showed that of the approximately 3590 tonnes of zinc entering Puget Sound, a fjord-like estuary in the northwestern United States, 45% came from rivers (both natural and anthropogenic), 24% by advective transport, and 23% from atmospheric input.

It was found that smelter operations release zinc and other metals into the environment. High metal concentrations can be found in the leaf litter for a distance of up to 40 km from the smelters. The metals are mobilized quite easily from this leaf litter, probably owing to the action of organic acids present in the decaying litter (Bolter *et al.* 1975).

On a global basis it has been estimated that in 1975 the total zinc emissions to the atmosphere from anthropogenic sources were approximately 314 000 tonnes, or approximately 5.6% of the global zinc production in the same year. This was more than 7 times the zinc input to the atmosphere from natural sources. The anthropogenic sources of zinc emissions to the atmosphere, on a global scale, are primary zinc production (32%), wood combustion (24%), waste incineration (12%), and iron and steel production (11%) (Nriagu 1979).

In the United States it has been estimated that the total air emissions during 1969 were approximately 145 000 tonnes, which represented 11% of the primary and secondary production of zinc or 8.9% of the zinc consumption during the same year. The main sources of zinc air emissions in the United States were metallurgical processing of zinc (31.3% of the total zinc air emissions in the U.S.), production of iron and steel (30%), incineration of refuse (18%), and end-product uses such as zinc alloys, coating, brass, bronze, zinc oxide manufacture and uses (15%) (Sittig 1975).

The atmospheric emissions of zinc in Canada in 1972 were estimated at 7396 tonnes or approximately 0.6% of the zinc production or 6% of the zinc consumed in Canada in the same year. The main sources of atmospheric zinc in Canada were estimated as follows: primary iron and steel production (36.4% of the total air emissions of zinc), primary copper and nickel production (31%), primary zinc production (10.2%), transportation (10.7%), fuel combustion-stationary sources (1.8%), solid waste incineration and mining operations (1.7% each) (Brown 1976a; Environment Canada 1976a,b).

The burning of fossil fuels is a major source of many metals to the environment. This does not seem to be the case for zinc. The concentration of zinc in coal has been estimated at about 4 to 60 mg/kg (Demayo *et al.* 1979). The world production of anthracite in 1977 amounted to

approximately 185 million tonnes. The 1977 world production of bituminous coal and lignite totalled an estimated 3242 million tonnes (U.S. Bureau of Mines 1978, pp. 38-41). Assuming that an estimated 15% of the bituminous coal and lignite production was used for coke, it leaves an estimated 2940 million tonnes of the three types of coal for space heating, electric utilities, and industrial consumption. Assuming a zinc concentration of 10 mg/kg, the coal burned in 1977 contained an estimated 29 400 tonnes of zinc. If the zinc concentration in the fly ash resulting from the burning of coal is approximately 100 mg/kg (Demayo *et al.* 1979), one can calculate that around 1100 tonnes of zinc are released annually to the atmosphere, 20 000 tonnes are used as landfill, and another 5000 tonnes are incorporated in concrete and asphalt manufacturing. The total of around 26 000 tonnes is small compared with the amount released into the environment by the primary zinc production.

In the Walker Branch watershed, Oak Ridge, Tennessee, where the soils had an average zinc concentration of 458 mg/kg (world average for similar soils is 50 mg/kg), it was concluded that the atmospheric zinc input from the stack emissions of coal-fired steam plants was the main source. The average watershed retention for zinc was calculated at 73% (range of 50% to 89%) (Lindberg *et al.* 1975).

The zinc concentration in petroleum products has a wide range (Demayo *et al.* 1979). Using a concentration of 1 mg/kg and considering the world consumption in 1974 of 2743 billion tonnes (Skinner 1976, p. 676), the total amount of zinc in the petroleum products is approximately 2700 tonnes. If the emission factor is about 10%, then approximately 270 tonnes of zinc will reach the atmosphere by the burning of petroleum products.

Data quoted by Hem (1972) showed a range for the yearly rainfall deposition rate of zinc in the United States of 2.4 to 595 mg/m^2, the higher values prevailing in the eastern United States, and an average zinc concentration in rainfall of 0.107 mg/L. The median concentration of zinc in filtered (0.45 μm) water samples from lakes and rivers of the United States quoted in the same publication was 0.020 mg/L, the implication being that rainfall might be a major source of zinc in surface waters.

A compilation of the concentration of various metals in precipitation showed that zinc values ranged from less than 0.001 mg/L at Resolute (Northwest Territories) to 0.311 mg/L in Sweden. The mean value for the zinc concentration in precipitation in the United States was estimated at 0.110 mg/L. In the smelting region of northern Ontario the concentration ranged from 0.030 to 6.8 mg/L (Kramer 1976).

Precipitation collected in the Sudbury (Ontario) region had average zinc concentrations of up to 0.0709 mg/L (Beamish and Van Loon 1977). The zinc extractable concentration in precipitation collected in the Lake Erie basin had geometric means of 0.026 to 0.062 mg/L depending on the season and especially on the type of sampler used. The bulk precipitation input to Lake Erie was estimated at 1000 tonnes/year or approximately 39 mg/m^2.a (Kuntz 1978). This value is much smaller than the results obtained by Kemp and Thomas (1976) for the same lake. Their estimated inputs at the six sampling stations in Lake Erie ranged from 93 to 593 mg/m^2.a (anthropogenic) and from 57 to 276 mg/m^2.a (natural). The anthropogenic and natural inputs at the three sampling locations in Lake Huron were estimated at 7 to 57 mg/m^2.a (anthropogenic) and from 12 to 17 mg/m^2.a (natural) (Kuntz 1978). The zinc inputs to Lake Ontario were estimated at 109 to 221 mg/m^2.a (anthropogenic) and 29 to 48 mg/m^2.a (natural). Another mean areal deposition rate for zinc in the Lake Ontario basin was calculated at 505 mg/m^2.a (Shiomi and Kuntz 1973). The mean concentration of zinc in precipitation was 0.080 mg/L, and apparently in this case it was not related to the degree of urbanization. From these values it was calculated that 994 tonnes of zinc enter Lake Ontario via areal deposition, which was about 58% of the estimated Niagara River zinc loading. Data from California coastal basins quoted by Kemp and Thomas (1976) showed the anthropogenic zinc input at 21 mg/m^2.a and the natural input at 52 mg/m^2.a.

In the vicinity of St. Andrews (New Brunswick) the precipitation (rain and snow) had an average zinc concentration of 0.0356 mg/L and the deposition rate was calculated at approximately 37.2 mg/m^2.a (Zitko and Carson 1971).

In a study of the Walker Branch watershed, Oak Ridge, Tennessee, the zinc concentration in rain water ranged between 0.0176 and 0.0612 mg/L. During the 14-month study, the monthly deposition rate ranged between 1.68 and 7.16 mg/m^2 with an average of 3.93 mg/m^2 (or 47 mg/m^2.a). Approximately 90% of the deposition was wetfall input. This rate was relatively low when compared with the average monthly zinc input by rain at 32 stations in the U.S. of 7.44 mg/m^2 or in the U.K. of 10.1 mg/m^2, quoted in the same study. The watershed retained 73% to 75% of the zinc input; the difference (25% to 27%), which was removed by the stream water, was mainly (≈90%) in a dissolved form (Andren *et al.* 1975).

Comparison of the areal input of heavy metals in a rural setting with that in an industrialized sector (Gary, Indiana) showed significantly greater input of Zn, Cd, Pb, and Fe for the latter system. The deposition rates for zinc ranged from approximately 29 to 97 mg/m^2.a in the rural

area, and 157 to 481 mg/m^2 in the industrialized area (Peyton *et al.* 1976).

In the lead-producing district of southern Missouri, monthly zinc deposition rates on a farm located at 800 m from a smelter were between 1.4 and 16.2 mg/m^2 (average 11.1 mg/m^2 or 133 mg/m^2.a). The corresponding range on a control farm was 1.28 to 1.85 mg/m^2 (average 1.63 mg/m^2 or 20 mg/m^2.a).

Data collected by Bradford (1977) also show that the atmospheric deposition of zinc is greater in industrial areas than in open spaces. In open space areas zinc deposition was approximately 0.074 g/curb km.d and 40 g/curb km.d in industrial areas. Beavington (1977) reported deposition rates (rain and dry deposition) ranging from 57 mg/m^2.a in a rural setting to 1260 mg/m^2.a at a site near a smelter complex (copper smelter and steel works) in Australia. In a large urban-industrial area (St. Louis) the median atmospheric wet deposition rates for zinc were between 10 and 57 mg/m^2.a, whereas the dry deposition rate was between 5 and 26 mg/m^2.a. Atmospheric emissions were the most important source of zinc at the surface (Huff 1976).

Other Anthropogenic Sources of Zinc to the Environment

In a hypothetical case study, Pitt and Field (1977) estimated that the storm water from a city of 100 000 people carried 6 tonnes of zinc per year and, if untreated, it could contribute a significant amount of pollution to the receiving waters. The authors also estimated that in order to protect the beneficial uses of the receiving water (in this case certain aquatic organisms) 97% of the zinc contained in the urban runoff would have to be removed by treatment.

In the Los Angeles region it was estimated that the zinc emission rate from large municipal wastewater plants (Los Angeles City, Los Angeles County and Orange County) was approximately 1100 tonnes per year, but the estimated aerial fallout in the area was only 150 tonnes/year or 410 kg/d. During a forest fire the aerial fallout of zinc increased almost three times to 1200 kg/d (or 44 mg/m^2.a) (Young and Jan 1977).

It was estimated that 1780 kg/d (or 650 tonnes/year) of zinc entered the sewage treatment plants of New York City and that 42% of this amount was of residential origin, 31% from runoff, 13% from electroplaters, 7% from the water supply itself, and the rest from other industrial sources. It was further estimated that New York City sources discharged to the harbour approximately 4970 kg/d (or 1810 tonnes/year) of zinc of which 63% was from runoff, 23% from treatment plant effluents, and 14% as untreated wastewater. The weighted average concentration of zinc in these discharges was estimated at 0.62 mg/L. In addition, approximately 620 kg/d (or 225 tonnes/year) was discharged into the harbour as sludge. The total input of zinc to the New York City harbour was, therefore, around 2000 tonnes/year, all from anthropogenic sources. The harbour waters had an average zinc concentration of 0.15 mg/L, while the concentration in the ocean water was 0.005 mg/L (Klein *et al.* 1974). For comparison, approximately 10% of the input to Lake Erie was estimated as coming from sewage discharges (Nriagu *et al.* 1979). The zinc concentration in the influents and effluents of 20 Ontario sewage treatment plants averaged 1.12 and 0.29 mg/L, respectively (Atkins and Hawley 1978, p. 384).

On a global basis it was estimated that the zinc input into the oceans from the industrial world's municipal wastewaters was approximately 100 000 tonnes/year, which represents approximately 14% of the zinc input to the oceans through natural weathering (Galloway 1979).

A list of zinc concentrations in various process wastewaters has been compiled by Sittig (1975). In concentration terms some wastewaters have very high values, e.g., bright mill wastes (metal processing), 40 to 1463 mg/L; wire mill pickle, 36 to 374 mg/L; rayon wastes, 250 to 1000 mg/L. The concentration of zinc in effluents from textile mill dyehouses was also high; it ranged from 0.10 to 58.0 mg/L, the 90th percentile being 4.40 mg/L (Netzer *et al.* 1975).

A mass balance for zinc and other metals on a 7.4-km stretch of the Saddle River near Lodi, New Jersey, gave negative results, indicating that the amount of metal removed from the system exceeded the amount flowing into the system. The negative mass balance for zinc amounted to about 235 kg/km^2.a or about 0.640 mg/m^2.d (Wilber and Hunter 1977). The average zinc concentrations in the Saddle River were 0.038 mg/L, 0.044 mg/L (rainwater), and 0.470 mg/L (stormwater). No conclusive answer was obtained regarding the quality of the stormwater in relation to land use, although in general the metal loadings decreased with increased percentage of residential land use. Wisseman and Cook (1977) reported that Wegato Lake (Washington) was accumulating zinc and also lead from street surface runoff in its sediments.

Another potential source of zinc to the environment is the "blowdown" from cooling towers (the "blowdown" is that fraction of recirculating cooling water which is discharged either continuously or intermittently in order to control the concentration of various substances, mainly inorganic salts, that accumulate in the cooling water). Zinc is commonly used as an anodic inhibitor in cooling tower treatment. Average zinc concentrations of 2.1 to 8.25 mg/L were measured in the blowdown water from towers where

zinc was used. In towers where zinc was not used, the mean zinc concentration, which was accumulated either from the air or from corrosion within the system, ranged from 0.0085 to 0.405 mg/L (Stratton and Lee 1975).

In a study in the lower Fraser Valley it was concluded that industrial and commercial land use resulted in much higher Zn (and Cd, Cu, Hg, and Pb) concentrations in stream sediments. Thus the zinc concentration in stream sediments from industrial, commercial and some residential areas averaged 181 mg/kg (range, 51.6 to 408 mg/kg), whereas in open space and residential areas the average was only 50 mg/kg (range, 27 to 68 mg/kg) (Hall and Fletcher 1974). Similarly, an average enrichment factor of 3.5 was reported for the zinc concentration in the bottom sediments from Lower Saddle River compared with locations upstream of the urban centre of Lodi (Wilber and Hunter 1979).

The concentrations of zinc (and other metals: Cd, Ni, Pb) in roadside soils and grasses decreased with the distance from the traffic. Zinc is present in motor oils and motor vehicle tires (Lagerwerff and Specht 1970).

Dredging of sediments at Port Stanley on Lake Erie did not result in any significant increase in the concentration of zinc in the sediments or in the pore water. The zinc concentration did increase, however, in the water column from an average of around 0.008 mg/L before and during dredging to 0.035 mg/L after dredging (Sly 1977). The corresponding pore water mean zinc concentrations were between 0.0058 and 0.010 mg/L and the sediment mean zinc concentrations were between 54 and 82 mg/kg. A similar survey conducted at Bronte Harbour on Lake Ontario did not show any increase in the zinc concentrations in the sediment, pore water or water column before, during or after dredging. The concentration values were in the same range as those from Port Stanley. In leaching experiments with sediments from Hamilton Harbour and Lake St. Clair, very little zinc, 0.06% to 0.27%, was released after 24 to 48 h. The sediment contained 4160 mg Zn/kg.

Brannon *et al.* (1978) measured the release rate of zinc from a series of dredged sediments from several places (harbours, rivers, waterways) in the United States. The release rate ranged from 0.083 to 0.41 mg/m^2.d; total sediment zinc concentrations, from 1.6 to 1505 mg/kg, and concentrations of interstitial water, from 0.001 mg/L to 0.86 mg/L (as extractable zinc). For an overlying water column of 10 m in depth and completely mixed, the release rates quoted above would mean an addition of 0.0083 to 0.041 µg/L.d.

Zinc was released from lake sediments under aerobic conditions when nitrilotriacetic acid (NTA) in concentrations of 50 to 100 mg/L was added to the water. At NTA concentrations of 0 to 25 mg/L the zinc concentrations in water were between 0.02 and 0.18 mg/L. At NTA concentrations of 50 and 100 mg/L the zinc concentrations in water were around 1.8 and 1.4 mg/L, respectively, while under an aerobic condition the highest zinc concentration attained was 0.05 to 0.06 mg/L at 50 to 100 mg NTA/L, respectively (Singer 1975).

Under static flow conditions EDTA (ethylenediaminetetraacetic acid) at a concentration of 1.0 mg/L significantly increased the concentration of zinc (also Fe, Mn, and Pb) above contaminated lake sediments. NTA (nitrilotriacetic acid) and TPP (sodium tripolyphosphate) at concentrations of 0.2 and 1.0 mg/L, respectively, also increased the concentration of zinc and iron in the water, but to a smaller extent. In the flow-through experiments no effects were observed with the chelating agents at concentrations of 0.2 to 5.0 mg/L, perhaps with the exception of the zinc and EDTA pair. Little or no effect was observed in the rate of uptake of metals by chironomids in the presence of various chelating agents (Barica *et al.* 1973).

Forms of Zinc

The normal valence states of zinc are Zn(0) and Zn(II). Compounds of Zn(I) do not occur under normal conditions, although ZnH and ZnX (X=Br, Cl) are known as spectroscopic species (Aylett 1973). Zinc can also form organozinc compounds such as ZnR_2 (R=Me, Et, n-Pr, n-Bu, n-pentyl, vinyl, Ph, etc.) or MeZnX (X=Br, Cl). Zn(II) also forms complexes with anionic, cationic, neutral, or more complex ligands (Aylett 1973). The zinc complexes formed with humic acid had the lowest stability constants when compared with the humic acid complexes of lead, copper and cadmium (Guy and Chakraborti 1976).

According to Wood (1974), zinc (also lead and cadmium) cannot be methylated in the environment as are, for example, mercury or tin. The methyl group from a vitamin B_{12} derivative (which is the only methylating agent capable of methyl transfer to Hg^{2+}) cannot be transferred to Zn, Pb or Cd. Also the alkyl-metals of zinc, lead and cadmium are unstable in aqueous systems.

In natural waters zinc probably exists as the simple hydrated ion, inorganic compounds (e.g. $ZnCO_3$), stable organic complexes (e.g., Zn-cysteinate), and adsorbed onto or occluded in inorganic (Zn^{2+}–clay) or organic colloids (Zn^{2+}–humic acids). The fraction of zinc in each of these species varies with factors such as pH, the total amount of

zinc in water, the presence of other metal ions, organic and inorganic compounds, etc. (Florence and Batley 1977).

The pH and ionic strength were found to strongly affect complexation of zinc (and other metals: Cu, Cd, Pb) by water-soluble organic acids extracted from leaf litter or found in soil. The complexation increased with the increased pH. Increased ionic strength (KCl) decreased metallo-organic complexation both by increasing competition for complexing sites and by creating chloride complexes (Butz 1976).

Model calculations using measured dissolved concentrations in water samples from Lake Celyn (North Wales) (pH, 6.2; humic ligand, 1.2; Zn, 0.18; Mg, 10; Ca, 26; Mn, 0.35; Ni, 0.02; Co, 0.017; Cu, 0.01; Cd, 0.0036; and Hg, 0.00035 μmol/L) showed that 88.8% of the zinc was in the form of free ion (Zn^{2+}), 7% complexed by the humic ligand, 3.1% as bicarbonate, 0.6% as carbonate and 0.5% as sulphate (Mantoura *et al.* 1978). Similar results were obtained for other metal ions: Mg^{2+}, 98.2%; Ca^{2+}, 97.8%; Mn^{2+}, 90.6%; and Cd^{2+}, 92.8%. In contrast, 100% of the Cu and Hg were complexed by the humic ligand. Nickel and cobalt occupied an intermediate position with 69.6% and 76.0% as free ions, respectively (bicarbonate, carbonate and humic complexes represented significant percentages in this case). The calculations also predicted that most, 75.2%, of the humic ligand will not be complexed with the metals present, at the concentrations and the pH listed above.

Model calculations for fresh waters in which both humic substances and inorganic ligands were considered showed that at pH <7 Zn^{2+} was the dominant species, followed by $ZnHCO_3$, $ZnCO_3$, humic complexes, and $ZnOH^+$. As the pH increased, the concentrations of $ZnCO_3$, Zn-humic substances, and $ZnOH^+$ also increased, however, the concentration of Zn^{2+} and $ZnHCO_3$ decreased. A decrease in alkalinity values favoured the free metal ion, while increased pH and increased concentration of humic substances favoured the formation of humic complexes. For example, at pH 6.5 and a concentration of humic substances of 20 mg/L, 8.3% of the zinc was in humic complexes. At a pH of 8.09 this percentage rose to 64.7. The dissolved zinc concentration, which was also calculated by the model from the solubility of zinc silicate (willemite-Zn_2SiO_4), decreased from approximately 20 mg/L at pH 6.5 to approximately 0.06 mg/L at pH 8.09 (Wilson 1978).

Model calculations for seawater showed that at pH 7, 51% of the zinc remained as uncomplexed Zn^{2+}, 19% as $ZnCl^+$, 10% as $ZnSO_4$, and 8% as $ZnCl_2$. At pH 8.1, the dominant species were $Zn(OH)_2$ (62%), Zn^{2+} (17%), $ZnCl^+$ (6.4%), and $ZnCO_3$ (5.8%) (Zirino and Yamamoto 1972). In these calculations the metals were considered to be only in the divalent state and polynuclear complexes; mixed ligand complexes and organic chelates were not considered. Using lower stability constants for $Zn(OH)_2$ and $ZnCO_3$, Mantoura *et al.* (1978) calculated the following zinc species in seawater have a salinity of 35‰ and a pH of 8.1: 47% Zn^{2+}, 20% $ZnCl^+$, 10% $ZnCl_2$ and 10% $ZnSO_4$.

A theoretical model investigation of chemical forms of zinc in a mixture of fresh water and seawater showed that at a pH below 7.5 approximately 65% to 95% of the zinc was in the form of free zinc ions (Zn^{2+}). The lower value corresponded to 100% seawater and the higher value, to 100% fresh water. In fresh water, the bicarbonate and sulphate ions were the important ligand species. Soon after seawater was added to the mixture, the chloride ions became the dominant ligand. The chloro ligand was also dominant in fresh water-brine mixtures. In this case, the higher order associations (Cl_2, Cl_3, Cl_4) became much more important than in fresh water-seawater mixtures (Long and Angino 1977).

Good positive correlations were obtained between the mean dissolved (0.45-μm filter) concentrations of Zn with Mg, Cu, Ni, and Cr in a study of the tributaries to Lake Michigan (Robbins *et al.* 1972). The zinc (also Cd, Pb, and Cu) concentration was measured by differential pulsed anodic stripping voltammetry (DPASV) in water samples from the Rhine River at pH 7 and from the North Sea at pH 8.1. These concentrations were compared with the concentrations in the same samples at pH 6.1. The concentration measured at the higher pH represented 40% of the zinc concentration measured at the lower pH. Part of the difference was attributed to organically bound ions (Duinker and Kramer 1977).

The investigation of the distribution of zinc and other metals between coarse particles (>0.15 μm), colloidal particulates (size between 0.01 and 0.15 μm) and dissolved solids (<0.01 μm) in stream water showed that although the dissolved phase had the lowest zinc concentration, it contained the highest percentage, approximately 75.1%, of the zinc in the samples; 24.4% was in the coarse particulates, and only 0.5% was found in the colloidal phase, which had the highest zinc concentration (Perhac 1972).

Florence (1977), in analyzing fresh water and tap water samples, reported that no zinc was associated with inorganic colloids and that very little zinc was associated with organic colloids. Most of the zinc was divided between labile ionic species and stable inorganic form.

Hart and Davies (1977) investigated the physicochemical forms of several trace metals in the water and in the interstitial water of the sediment from an urban creek in Melbourne, Australia. In the bulk water the filterable (0.4-μm Nucleopore filter) zinc had a concentration of

0.090 mg/L, of which approximately 40% was in free ionic forms or labile complexes (complexes whose stability constants were less than those of the combination of metal with the ion exchange resin Chelex used in the analytical procedure). The other 60% of the zinc was in complexes smaller than 2 nm in diameter (this size would exclude most of the colloidal iron and manganese oxides, and perhaps humic acid complexes). In the interstitial water, zinc had a concentration of 0.4 mg/L of which only about 26% was in the form of free ions and labile complexes, 15% as complexes of a size smaller than 2 nm and 59% as other inorganic and organic complexes, and associated with colloidal forms.

Average zinc concentrations of 0.057 to 0.080 mg/L, divided almost equally between the filterable (0.45 μm membrane filter) and nonfilterable fractions, were reported for the Grand Calumet River (Romano *et al.* 1977). Brown (1977b) measured zinc (also copper and iron) concentrations in water, sediment and invertebrates collected from the River Hayle. In water, at least 80% of the zinc was in the soluble form (0.45 μm), while at least 70% of the concentrations of the other two metals was associated with the particulate fraction.

In the Susquehanna basin in New York State it was determined that around 40% of the zinc was transported in a dissolved phase (McDuffie *et al.* 1976). Data obtained by Carpenter *et al.* (1975), also for the Susquehanna River, showed that the total metal concentrations (Zn, Mn, Fe, Cd, Cr, Co, Cu, Ni) were correlated with the discharge of the river and with the total suspended solids, thus indicating that especially in periods of high discharge, most of the metals are carried in the suspended materials phase. The dissolved fraction was significant during the period of peak concentrations which occurred from January to March. During this time decaying organic matter was abundant in the river, so that the high concentrations may be the result of the binding of zinc (and other metals) to organisms.

In snowpack samples collected in the Santa Fe Ski Basin (New Mexico) most and sometimes all of the zinc was found in the particulate matter (this was also true for lead and copper). Almost 100% of the zinc in the stream was found in the particulate matter (Moore *et al.* 1978).

Delfino (1977), in a study of the Mississippi River, found that the concentrations of Zn, Fe, Mn, Cu, P, COD, and suspended solids increased with increased discharge. Similarly, Jennett *et al.* (1977), who monitored the water quality of several creeks in the Viburnum Trend or New Lead Belt of Missouri, a region of mining, milling and smelting operations, found that during peak runoff periods following a storm, the increases in the dissolved metal concentrations were very small, but the total concentrations and the suspended solids increased abruptly. Probably soil particles had been washed directly into the streams. Jennett *et al.* (1976) reported that in the Crooked Creek watershed, which drains a region containing the world's largest lead-zinc mining operation, zinc was generally transported in a dissolved form except during periods of extremely turbulent runoff. In a study of the River Ystwyth (Wales) the peak zinc concentrations occurred during low flow periods and at the onset of increasing runoff. This "flushing" effect was followed by a "dilution" effect, i.e., the zinc concentration decreased during the runoff event. In terms of zinc loadings, however, the highest values were reached during storm runoff periods (Grimshaw *et al.* 1976). The concentration of zinc and other metals in Lake Carl Blackwell (Oklahoma) was also higher after periods of rainfall, suggesting that land runoff is an important source of metals in the water (Sias and Wilhm 1975).

In tests with zinc and copper solutions prepared in the laboratory it was shown that the toxicity to fish of a given concentration of the metal ion decreased as the concentration of added suspended solids increased. The suspended solids added consisted of humus-tank solids from a sewage plant treating a detergent-free domestic sewage. The concentration of the soluble zinc, copper and cadmium fell quickly after the preparation of the solids-metal salt solution mixture (Brown 1976b).

A study of Lakes Michigan, Ontario and Mendota showed that zinc was more concentrated in the surface microlayer (upper 0.3 mm of the lake water) than in the bulk of the lake by a factor of 2.8. The presence of a surface organic microlayer favoured this enrichment. Most of the excess zinc in the surface microlayer was probably in particulate form of atmospheric origin (Elzerman 1977). In contrast, surface samples from Lake Carl Blackwell (Oklahoma) averaged 0.010 mg/L (range of 0.002 to 0.042 mg/L), and bottom samples averaged 0.028 mg/L (range of 0.005 to 0.097 mg/L) (Sias and Wilhm 1975).

The transfer of metals between bottom materials and the water above them is a complex process depending on a multitude of factors such as the dissolved oxygen concentration (aerobic or anaerobic conditions), the nature and the concentration of heavy metals, the organic and inorganic ligands present, the pH, and the particle size of the bottom sediments (Lee and Mariani 1977; Lu and Chen 1977). Some of the individual processes which may be involved in this transfer are surface exchange, diffusion exchange, precipitation, complexation and dissolution (Jenne and Luoma 1977).

Aeration for up to 5 days of anaerobic sediments from a tributary of the Rhine River led to an increased dissolved zinc concentration because of the release of

organically bound metal. When the aeration continued for up to 20 days the dissolved zinc concentration decreased, probably owing to the precipitation of the released metal in the form of carbonate. Finally, a third aeration phase of up to 40 days again increased the dissolved zinc concentration, probably because of the formation of easily soluble bicarbonate (Müller and Schleichert 1977).

Reducing (anaerobic) conditions for approximately two months decreased the concentration of zinc in the overlying water at the interface between seawater and polluted surficial sediments. The initial zinc concentration in the water ranged from 0.00038 to 0.00215 mg/L and from 115 to 415 mg/kg in the sediments. The decrease was probably caused by the formation of insoluble ZnS. Oxidizing conditions (dissolved oxygen, 5 to 8 mg/L) increased the concentration of zinc (also of Cd, Cu, Ni, and Pb) in the water, probably owing to the change from metallic sulphide to the more soluble carbonate, hydroxide, oxyhydroxide, oxide, or silicate (Lu and Chen 1977). Calculations based on a pure inorganic model (organic complexation of metal ions was not considered) gave similar results. Under reducing conditions, ZnS was the main zinc species (over 90%); under oxidizing conditions and depending on the pH, Zn^{2+}, $ZnCO_3$ and $ZnSiO_3$ accounted for over 90% of the total zinc, with $ZnSO_4$ and $ZnCl^+$ accounting for a few per cent (Morel *et al.* 1973).

Lee (1975) has reviewed the role of manganese and iron oxides, which are nearly ubiquitous in suspended solids and sediments, as partial coatings on other minerals and as discrete oxide particles. He supported Jenne's proposal (1968) that these oxides act as a sink for trace metals (Co, Ni, Cu, Zn). The various degrees of sorptive activity of the oxides depended among other things on their age. The non-stoichiometry of the reactions between the hydrous metal oxides and the metals made simple solution equilibria and chemical kinetics inapplicable to these systems (Boyle 1968, p. 68).

Farrah and Pickering (1977) studied the removal of zinc (also Cu, Pb, and Cd) from aqueous solutions by clay suspensions. They concluded that the amount removed was a function of the nature of the clay (kaolinite, illite, or montmorillonite), solution pH, concentration of competing cations, the nature and the concentration of any ligands present, and the order in which the various species, i.e. clay, competing ions and ligands came into contact. At initial concentrations of 1.7×10^{-4} mol/L (or approximately 11 mg/L for Zn) the amount of metal adsorbed by clay increased linearly with pH in the range 3.5 to 6.5. In acidic solution (pH <5) most of the metal ions stayed in solution. The formation of stable cationic complexes may have prevented the precipitation of the sparingly soluble hydroxy species which become associated with the clay in alkaline media. Also, protonated ligands may have competed for adsorption sites, thus reducing the sorption of the metal ions on the clay materials. As the pH increased to about 7 (6.9 to 7.9 for zinc) most of the metal was precipitated and/or sorbed. The formation of sparingly soluble species $M_x(OH)_y^{x+}$ for divalent metal ions has been postulated by several authors (see, for example, Farrah and Pickering 1977). The presence of anions that form salts of low solubility should also have reduced the concentration of metal ions in solution. The ability of clays to adsorb cations as well as anions produced different results for different metals.

Frost and Griffin (1977) found that the removal of zinc, copper and cadmium from a municipal landfill leachate by kaolinite and montmorillonite increased with increased pH and concentration of the metal ions in the leachate. At low pH values adsorption was the dominant mechanism. As the value of the pH increased above 5.5, precipitation of species such as $Cu(OH)_2$, $Zn(OH)_2$, and $CdCO_3$ became the dominant mechanism for removal. Montmorillonite sorbed approximately five times more metal from solution than kaolinite. The reverse process, i.e., the release of metals from the particulates, can take place by one of three mechanisms: (i) ion exchange, where a cation from the solution changes place with an adsorbed cation, (ii) solubilization of the matrix, and (iii) decomposition of the matrix. The release of metal from sediments via decomposition may be an important mechanism for the hydrous oxides of iron and manganese (Guy and Chakrabarti 1976). Griffin *et al.* (1977) concluded that the mobility of Zn, Cu, and Cd in soils or clay minerals is dependent upon solution pH, ionic strength, and cation exchange capacity of the soils or clay minerals. At pH >7 precipitation becomes much more important than cation exchange in the removal of these metals from solution.

In laboratory experiments freshly prepared iron and aluminum gel suspensions adsorbed an increasingly greater fraction of the Zn^{2+} ions with increasing pH. For example, from a solution containing 0.0065 mg Zn/L, approximately 1.5% was adsorbed at pH 3.96 in 14 h by an iron gel, 57.1% at pH 5.06, and 97.8% at pH 5.99. The amount of zinc adsorbed also increased with the increase in the weight of the gel, and aged gels were found to be more reactive than fresh gels (Kinniburgh *et al.* 1977). A strong increase in the adsorption of zinc (also Cu and Pb) ions from solution onto various oxides, minerals and soils was observed at pH 5 to 6 (Huang *et al.* 1977; James and MacNaughton 1977).

In a study of the surficial sediments from the Fraser River delta it was found that zinc concentrations in the minus 80-mesh fraction, ranging from 52.7 to 77.1 mg/kg, showed a very strong negative correlation with the percent-

age of sand in the sample. Strong positive correlations were found between the zinc concentration on one hand and the loss on ignition, copper, iron, manganese, lead and cobalt concentrations on the other hand (Grieve and Fletcher 1976). This was consistent with the role of a sink for trace metals which had been suggested for the iron and manganese oxides that form a coating on sediment particles (Lee 1975; Jenne 1968). Foster *et al.* (1978), in studying the fate of various metals in an acid mine stream, reported that loss of zinc occurred as the water travelled towards the estuary and that the loss was due to adsorption onto hydrated ferric oxide at pH values above 6.

It has been reported that in the interstitial water of marine sediments all the zinc was bound to dissolved, humic-type materials, while in the dry sediments 15% to approximately 30% of the zinc was bound to humates. The zinc concentrations in the sediments ranged from approximately 48 to 130 mg/kg. It was concluded that the polymeric organic material dissolved in the interstitial water was a precursor of the sedimentary humates. The chelating and adsorbing abilities of the dissolved organic matter were probably the main factors in the leaching of zinc and other metals from minerals (Nissenbaum and Swaine 1976). In a representative sediment sample from the Lower Rhine around 90% of the zinc was in the form of carbonate and around 5% as humate (Förstner 1977).

When sediments contain low amounts of organic materials - up to 12% loss on ignition (LOI) - these materials limit the concentration of zinc in the sediments. Above 50% LOI, the amount of zinc in the system controlled its concentration in the sediments. At LOI values between 12% and 50%, it was the chemistry of the system which controlled the distribution of zinc between various phases (Garrett and Hornbrook 1976).

Jackson (1977) found good correlations between the organic carbon content and the concentrations of zinc (also of Hg, Cu, Cd and Fe) in sediments from Clay Lake and Ball Lake (Ontario). Hall *et al.* (1976) reported excellent positive correlations of the zinc (also Cu and Pb) concentration in sediments with the organic matter and with the fine (<53 μm) particulates content of the sediments of the Brunette drainage basin in British Columbia. Similarly, Hunt (1975) reported good correlations between zinc and lead concentrations, and the organic matter content of sediments from Lake Champlain. Good correlations between the zinc concentration, and manganese concentration, percentage of clay and loss on ignition were reported for sediments of the tributaries of the Great Lakes (Hutchinson and Fitchko 1974).

Good positive correlations were found between the zinc concentration, and organic carbon, percentage of clay-sized particles and depth of the overlying water in sediments from the Fort Gibson reservoir in the Grand River system (Pita and Hyne 1975). Pezzetta and Iskandar (1975) also reported good positive correlations between zinc and other metal concentrations, and the organic carbon and the silt content of sediments at the mouth of Fox River (Green Bay area). They also found that the coal-fired electric power plant situated in the study area had a significant but localized effect on the distribution of metals in the sediments. Interestingly, the sediments closest to the plant had lower concentrations of metal (Zn, Cu, Cr, Hg), organic carbon and finer particulates than sediments located upstream from the power plant. This was explained by the jetting action of the thermal plume, which flushed out the fine particulates, increased the metal release from the sediments and increased the microbial decomposition of the organic matter. Loring (1976) reported that the dispersal of zinc in the Saguenay Fjord was controlled by the sedimentation pattern and sedimentation rate of the fine-grained inorganic and organic matter in the system.

In studying the sediments of the Willamette River (Oregon) Rickert *et al.* (1977) found that the <20-μm fraction enabled them to identify those segments of the river bed which were affected by pollution sources and also determine the "natural" background concentration of zinc (<145 mg/kg) and other metals in the sediments.

The minus 80-mesh fraction of the top 1 to 6 cm of the sediments of Lake Superior around Keweenaw Point had zinc concentrations from 29 to 150 mg/kg with a mean of 68.4 mg/kg, and this was strongly correlated with the copper concentrations (Smith and Moore 1972).

Steele *et al.* (1975) could not find any correlation between the zinc and other metal concentrations in water and the respective bottom sediments of the Buffalo River in northern Arkansas.

The Boundary Dam Reservoir in the southern Prairie region of Saskatchewan provides condenser cooling water used in thermal electric power generation. In a study of the reservoir, zinc and other metals, e.g., Pb, and Cd, showed a tendency to concentrate in the surface sediments in the downstream end of the reservoir. The zinc concentration in the surface sediments of Boundary Dam Reservoir and also of Lake Wabamun (a natural lake in northern Alberta whose waters are also used for the cooling of two power plants) were slightly higher than in other typical prairie lakes, probably because of emissions from the power plants (Allan and Richards 1978).

In aquarium studies, dissolved zinc ions extracted from the aqueous solution after 17 days concentrated in the top 2 cm of the bed sediment, which was the lowest

penetration depth of the several metals involved in the experiment, e.g., Co, Sr, and Cs (Gloyna *et al.* 1971).

Luoma and Jenne (1976) studied the biological availability of zinc, silver, cadmium and cobalt from six types of physicochemically different sediments (organic detritus, iron oxides, organically coated iron oxides, manganese oxides, inorganic carbonates, and biogenic carbonates) to bottom feeding clams *Macoma balthica*. Metal concentrations in soft tissues of the clam were compared with the metal concentrations extracted from the sediment by various methods. The biological availability of zinc was most closely estimated by 1 *N* ammonium acetate extraction or 1 *N* NaOH plus EDTA extraction. Other extraction agents such as weak acids (0.1 *N* HCl or 25% acetic acid), reducing compounds (1 *N* hydroxylamine hydrochloride in 0.01 *N* HNO_3, or sodium dithionite plus citrate), or oxidizing agents (e.g. 3% H_2O_2 plus citrate) gave poor correlation with the biological accumulation. They concluded that no single chemical extractant adequately described the biologically available fraction (to clams *Macoma balthica*) of zinc (also Cd and Co) from sediments.

Analysis of the sediments of the Saguenay Fjord (Quebec) showed that most of the zinc, 71% to 86%, was in the acetic acid insoluble fraction (detrital), mainly as sulphide minerals. In the non-detrital fraction most of the zinc was apparently found in the organic matter. Good positive correlations were obtained between zinc concentration (both detrital and non-detrital) and the mud, organic carbon, magnesium, copper and lead concentrations. Good negative correlations were obtained between the detrital and non-detrital zinc concentrations, and the sand and silica content of the sediments (Loring 1976).

RATIONALE

Raw Public Water Supplies

Zinc in the Human Body and Laboratory Animals

Zinc is one of the essential elements for human health and "... if one had to choose the most important (micronutrient) it would be zinc" (Schroeder 1974a, pp. 6-7, 115).

The exact role zinc plays in the human organism is not known. Zinc has been implicated as an essential element in enzymes and enzymatic functions, protein synthesis and carbohydrate metabolism (Halsted *et al.* 1974; Eichhorn 1975). In the rat, zinc appears to be essential for the synthesis of DNA, RNA and for amino acid metabolism, i.e., the incorporation of methionine into liver and kidney tissue proteins (Sandstead 1975; Hsu *et al.* 1969; Luckey *et al.* 1975). Among a series of metals analyzed by neutron activation in the DNA of calf thymus, zinc had by far the highest concentration (1450 mg/kg). Experiments have shown that zinc and other metals (Cu, Ag, Cd, Hg, Sn; but not Cr, Mn, Ni, Se, As, etc.) were incorporated into the cadmium-binding protein isolated from rat liver (Sabbioni and Girard 1977).

The utilization of nitrogen and sulphur in the animal body requires zinc. Zinc also plays a critical role in the processes of cell division and growth, and is apparently also involved in the metabolism of the pituitary and adrenal glands, and the gonads. Zinc is essential for spermatogenesis, formation of ova and in the nutrition of the fetus (Sandstead 1975). Zinc was present in the tissues of 4-week-old human embryos at concentrations of 2.6 to 3.0 mg/kg (wet basis). This concentration increased rapidly to 18.2 mg/kg in the fifth week and it almost levelled off afterwards, reaching 24.8 mg/kg at 78 days of age. This rapid increase suggested that the presence of zinc was essential in the early stages of development. On a per organ basis, the zinc concentration was highest in the liver. The livers of second trimester fetuses had a mean zinc concentration of 167.7 mg/kg of wet tissue, which was about 9 and 30 times the zinc concentration of the kidneys and brains, respectively (Chaube *et al.* 1973).

The estimates for the zinc content of adult man ranged from approximately 1.4 to 3 g (Sandstead 1975; Underwood 1971, p. 209; Buhler 1973). On a per kilogram of body weight basis it increased from approximately 20 mg/kg in the newborn to 30 mg/kg in the adults (Sandstead 1975). The whole body half-life of zinc was estimated at 933 days (Buhler 1973). The skin contained up to 20% of the total body zinc. On a concentration basis the muscle, liver, and kidney contained approximately 55 mg Zn/kg (fresh weight), and the prostate contained up to 850 mg/kg. The zinc concentration in semen and sperm was high and reached 2000 to 3000 mg/kg (Sandstead 1975).

On a dry weight basis the highest zinc concentrations were found in teeth, with a range of 58 to 992 mg/kg and a mean of 366 mg/kg. This was followed by prostate (mean 243 mg/kg), pectoral muscle (200 mg/kg), kidney (188 mg/kg), liver (169 mg/kg), etc. (Smith 1967).

Within cells from human tissues, zinc is found in metalloenzymes (e.g. carbonic anhydrase, alcohol dehydrogenase, alkaline phosphatase) as well as complexed with nonenzyme organic molecules (e.g., nucleic acids) (Sandstead 1975). Of the total zinc contained in human blood, 75% to 88% was found in the red cells, 12% to 22% in the plasma and 3% in the leukocytes (Underwood 1971).

Guinea pigs fed on a diet containing 45% cabbage grown on municipal sewage sludge and containing 224 mg

Zn/kg (dry weight) showed very little increase in the zinc content of various tissues when compared with a control group. The control cabbage contained 17 mg Zn/kg. For example, the zinc concentration in kidney rose from 95.2 to 116.2 mg/kg (dry weight), in liver from 85.9 to 98.9 mg/kg and in muscle from 36.3 to 46.1 mg/kg (Babish *et al.* 1979).

Zinc started to accumulate in the rat liver at dietary levels of 1000 mg/kg or higher. At a dietary level of 2000 mg/kg the zinc accumulated rapidly in the metallothionein in the liver and kidney. The accumulated zinc depleted rapidly when the rats were fed on a zinc-deficient diet (Chen *et al.* 1977). At dietary levels of less than 500 mg Zn/kg, zinc did not accumulate in tissues (Chen *et al.* 1977; Schroeder 1974a, p. 115). Studies with rats have shown that the body maintained its zinc balance by changing both the extent of intestinal absorption of dietary zinc and the rate of fecal excretion (Weigand and Kirchgessner 1978).

Zinc absorption occurs mainly in the small intestine, especially in the duodenum. A low molecular weight, zinc-binding ligand (ZBL) present in certain types of milk, e.g., human and rat, and in the intestine has been proposed as playing an important role in zinc absorption (Duncan and Hurley 1978). It was estimated that about 40% of the dietary zinc intake is absorbed by an adult (WHO 1978). A detailed zinc balance kept for one person showed a zinc retention of 5.1 mg/day, representing 38% of the dietary zinc ingested. The same retention of around 5 mg was also observed after the consumption of meals (oysters) with a high zinc content (59 and 75 mg) (Smith *et al.* 1976).

The absorption of zinc is influenced by such factors as age, and zinc, protein and calcium levels of the diet (Franz 1978). Experimental results with rats have shown mean absorption values ranging from 26.8% (soy-based infant formulas) to 66% (sweetened condensed milk) of the total zinc available in various types of milk (Johnson and Evans 1978). The intestinal absorption reached nearly 98% in zinc-deficient diets (10.6 mg Zn/kg of diet). The total daily intake averaged 0.110 mg of which 0.108 mg was absorbed. The absorption dropped to only 33.8% in a diet containing excess zinc (141 mg/kg of diet). In this case the total daily intake was 1.69 mg of which 0.57 mg was absorbed. The corresponding values for the "normal" diet containing 18.2 mg Zn/kg were as follows: absorption, 93.3% of the intake or 0.190 mg/kg from a total daily intake of 0.204 mg.

The zinc retention represented 72.5% of the intake in the zinc-deficient diet and dropped to 16% in the diet containing 141 mg Zn/kg. In absolute amounts, however, in the zinc-deficient diet the retention averaged 0.080 mg/d, and in the diet containing excess zinc the zinc retention was 0.267 mg/d. With the "normal" diet (18.2 mg Zn/kg) the body retained 0.138 mg Zn/kg or 68% of the intake (Weigand and Kirchgessner 1978). The peak daily retention of zinc in humans apparently depended very much on age and, in women, on pregnancy. During puberty the retention increases to approximately 0.7 to 0.8 mg/d. In pregnant women the retention increases from 0.55 to 1.0 mg/d depending on the stage of the pregnancy. In lactating women the daily retention of zinc reaches 3.45 mg/d (Sandstead 1975).

Considering zinc retention and elimination by the human body, it has been calculated that the total zinc required by the human body ranges from 1.1 mg/d in infants to 2.2 mg/d in childhood and adulthood, and to 2.8 mg/d at puberty. In pregnant women the zinc requirements are slightly higher, i.e. from 2.55 to 3.0 mg/d, and they reach 5.45 mg/d in lactating women (Sandstead 1975). In the United States a daily intake of 15 mg Zn was approved as "optional" (Schroeder 1974a, pp. 115, 128). To convert these zinc requirements to the amount of zinc ingested daily, the availability of zinc from the various foods must be considered.

The main intake source for zinc is the diet. Data summarized by Clemente (1976) showed that of the average daily zinc intake in Italy, estimated at 8.125 mg, over 98% came from the cooked diet, 1.5% from the drinking water and an almost negligible fraction through inhaled air. Schrauzer *et al.* (1977) have summarized the apparent dietary intake of several metals in 28 countries. The zinc dietary intake ranged from 4.6 mg/d (Taiwan) to 21 mg/d (New Zealand). The dietary zinc intake in Canada was listed at 14.6 mg/d.

Among various foods listed by Underwood (1971), oysters, which can contain up to 1000 mg Zn/kg, were the richest suppliers of zinc, followed by wheat germ (40 to 120 mg/kg). Sandstead (1975) and Schrauzer *et al.* (1977) have also summarized some of the data on the zinc content of various foods. Meat has a high zinc content, with concentrations ranging from 11 mg/kg in chicken breast to 64 mg/kg in roast beef (wet weight). Grains (wheat, oats, rye) contain 31 to 33 mg Zn/kg, nuts contain approximately 34 mg Zn/kg, and eggs, 20.8 mg Zn/kg. Wine can contain up to 5.6 mg Zn/L. Whole wheat bread contains around 10 mg Zn/kg, but it is probably not a very good source of zinc owing to the presence of phytate, which inhibits the gastrointestinal absorption of zinc. Vegetables contain between 2 and 7 mg Zn/kg (wet weight) and fruit, between 0.5 and 1.2 mg Zn/kg (wet weight) (Sandstead 1975; Schrauzer *et al.* 1977; Schroeder 1974a, pp. 119, 123).

In a survey of Canadian food, the zinc content of meat, fish and poultry was between 36.6 and 48.8 mg/kg (fresh weight); fruit contained between 0.7 and 1.1 mg/kg (fresh weight). The zinc content of other food ranged between these two extremes. Drinks contained 0.4 to 0.6 mg Zn/L. From these data the average daily intake of zinc from a typical Canadian diet has been estimated at 19.9 mg/d. The average daily requirement of zinc has been estimated at between 10 and 20 mg/person (Méranger and Smith 1972). Another survey (Kirkpatrick and Coffin 1977) found that a person's total daily intake of zinc from food in Canada is 15.55 mg. The zinc concentration (fresh weight basis) ranged from 0.58 mg/kg in drinks to 33.04 mg/kg in meat, fish and poultry.

Food processing, such as the refining of sugar, wheat or rice, leads to losses of zinc of 50% to 98%. Skim milk is an exception, since it retains 86% of the zinc content of whole milk (Schroeder 1974a, p. 121; WHO 1978).

Apparently "plant zinc" is less available for absorption by the human organism than "animal zinc." The formation of insoluble complexes of zinc and calcium with phytate (inositol hexaphosphate), mentioned before, in the gastrointestinal tract could be one reason for the lesser availability of "plant zinc." Another possible reason could be the binding of zinc by certain plant components: fibre, certain hemicelluloses, and amino acid carbohydrate complexes (Sandstead 1974). Experiments conducted with rats have shown, however, that only about 32% of the zinc contained in raw or cooked rat liver was absorbed through the intestine, whereas about 51% and 65% of the zinc contained in raw corn flour and cooked corn meal, respectively, were absorbed (Evans and Johnson 1977). No explanation was found for these rather unexpected results. In the same series of experiments, it was found that the zinc present in reconstituted dried milk and liquid infant formulas was less available than the zinc in the dried milk and dry formulas. Again, no explanation was found for these results. The study mentioned before on the dietary intake of several trace metals from 28 countries has shown that dietary zinc, cadmium, copper and chromium intakes were strongly associated, probably because of the similarities of the distribution in major food items (Schrauzer *et al.* 1977).

Zinc excretion occurs mainly via the feces and consists of unabsorbed dietary zinc and endogenous zinc secreted mainly into the small intestine via the pancreatic juice (Underwood 1971). With a "normal" diet, containing 18.2 mg Zn/kg or 0.204 mg/d, the fecal excretion of zinc in rats amounted to 12.7% of the intake. The body retained 0.138 mg/d or 68% of the intake. With a zinc-deficient diet of 10.6 mg Zn/kg, for an average total daily intake of 0.110 mg Zn, the fecal excretion amounted to 5.7% of the intake; and in a diet containing excess zinc, 141 mg/kg for a total zinc intake of 1.69 mg/d, the fecal excretion varied between 16% and 24% of the zinc intake. The urinary excretion of zinc increased much more slowly from a low of 0.0214 mg/d for the zinc-deficient diet to a high of 0.036 mg/d for the excess-zinc diet. Rats fed on the "normal" diet eliminated 0.0263 mg/d via the urinary tract (Weigand and Kirchgessner 1978).

Sandstead (1975) quoted data showing that the urinary excretion of zinc ranged between 0.4 and 0.5 mg/d, and the sweat excretion between 0.5 mg/d in infants and 1.5 mg/d in teenagers and adults. Larger than normal losses of zinc can occur via the gastrointestinal tract, the urinary tract or the skin as a result of certain pathological conditions such as steatorrhea, impaired tubular reabsorption or tubular secretion of zinc by the kidney, or excessive loss of fluids from burned surfaces (Sandstead 1975). Inflammation appeared to mobilize zinc from muscle and other tissues for transport to the liver. Higher urinary excretion of zinc has also been reported in diabetes. A significant increase in the excretion of the metal via the feces and urine was also found in rats fed on a zinc-deficient diet. This was accompanied by a depletion of the zinc accumulated in the metallothionein fraction in the liver and kidneys (Chen *et al.* 1977). Significant changes in the zinc concentration of plasma occur in various diseases. For example, the zinc levels of plasma are lower than normal in patients with atherosclerosis, malignant tumours, chronic and acute infections, untreated pernicious anemia, post-alcoholic cirrhosis of the liver, etc. (Underwood 1971).

Zinc Deficiency

The main cause of zinc deficiency seems to be an inappropriate diet, such as in places where the energy and protein intake is of plant origin. The zinc (and iron) in cereals is present as phytic acid complexes which are poorly absorbed by the digestive system (Kirchgessner *et al.* 1977). Intestinal malabsorption syndromes, excessive urinary excretion, and the medical use of oral or intravenous synthetic diets can also lead to zinc deficiency (Hambidge 1974).

Zinc deficiency produces a syndrome characterized by growth failure, delayed puberty, iron deficiency, hepatosplenomegaly and endocrine manifestations consistent with some degree of hypopituitarism (Sandstead 1975; Kirchgessner *et al.* 1977). Associated symptoms of zinc deficiency are the loss of hair, parakeratotic skin lesions, loss of appetite and distaste for food (dysgeusia), diminished taste acuity (hypogeusia), and general lethargy (Hambidge 1974; Kirchgessner *et al.* 1977). It has also been reported that zinc deficiency might be a factor in the etiology of the cancer of the esophagus and post-alcoholic cirrhosis of the

liver (Farnsworth and Kline 1973, p. 20; *The Ottawa Citizen* 1977; Gabrial and Newberne 1979).

Delayed wound healing has been found responsive to zinc treatment in some patients and animals, especially those who are zinc deficient. The exact mechanism of this action and whether or not zinc helps the wound healing in nutritionally well-balanced people are issues not yet resolved (Sandstead 1974, 1975; Chvapil 1974). Some cases of atherosclerosis were also found responsive to zinc treatment (Sandstead 1974; Underwood 1971). Schroeder (1974b) mentioned that zinc administered orally was beneficial in the treatment of occlusive atherosclerosis of legs and heart.

In rats, zinc deficiency during pregnancy resulted in decreased brain size and learning impairment (Sandstead 1975). Hambidge (1974) and Hurley (1976) quoted results which showed that with rats, early postnatal zinc deficiency impaired learning ability and that in female rats zinc deficiency led to impaired reproduction and teratogenic effects. Offspring of rats fed on a zinc-supplemented diet had a superior learning ability and were more active than rats from mildly zinc-deficient mothers. The *in vivo* synthesis of DNA in the liver and blood glucose homeostasis were impaired or depressed in zinc-deficient rats and rat embryos (Underwood 1971; Hurley 1976). Chromosome aberrations were observed in the liver tissues of zinc-deficient rat fetuses and in maternal bone marrow (Hurley 1976). Also in rats, dietary zinc deficiency, low food intake, reduced dietary protein content and endotoxin administration all reduced the plasma zinc concentration and the activity of plasma alkaline phosphatase, and increased the zinc uptake *in vitro* by cells of whole blood (Sandstead 1975; Chesters and Will 1978).

The activities of various zinc-containing or zinc-dependent enzymes change in cases of zinc deficiency (Underwood 1971). Thus it has been proposed that the effects of zinc deficiency are due to fundamental changes in the activity of enzymes and hormones and in the metabolism of proteins and nucleic acids (Kirchgessner *et al.* 1977).

The Toxicity of Zinc

The difference between the essential and toxic levels of zinc is large. There are indications that under normal conditions the serum zinc-binding proteins are not saturated with zinc. In circumstances where zinc is in excess, the excess is apparently bound by albumin (Smith *et al.* 1976).

The emetic dose of zinc ranges from 220 to 450 mg (Perrin and Agarwal 1976). The emetic dose of zinc in water ranges from 675 to 2280 mg/L (Sandstead 1975). In addition to vomiting, the symptoms of zinc toxicity include dehydration, electrolyte imbalance, stomach pain, nausea, lethargy, dizziness and muscular incoordination. Acute renal failure followed ingestion of $ZnCl_2$ (Halsted *et al.* 1974).

The occupational disease "metal fume fever" occurs in persons exposed to zinc or zinc oxide fumes or dust (Sandstead 1974; Perrin and Agarwal 1976). Its symptoms are pulmonary distress, fever and chills.

Hypertension was induced in rats fed on a diet containing 225 mg Zn/kg over a period of several months (Sandstead 1975). Weanling rats drinking water which contained 125 mg Zn/L for one year did not show a significant increase in the systolic pressure when compared with the control group. The drinking water of the control group contained 50 mg Zn/L (Perry and Erlanger 1974).

Schroeder (1974a, p. 115) mentions that oral doses of 150 mg Zn/d have been administered to patients without any toxic effects. Diets containing 2500 mg Zn/kg (as metal, chloride or carbonate) had no discernible effects on rats. Deleterious effects started to appear at levels of 4000 to 5000 mg Zn/kg of diet (Underwood 1971).

Zinc concentrations of up to 240 mg/L of full blood increased the activity of ALA-D *in vivo* and *in vitro*. Higher concentrations led to a decrease in the ALA-D activity (Schlipköter *et al.* 1975).

No correlation was found in an epidemiological study conducted in South Wales between neural tube defects and zinc concentration in drinking water (Morton *et al.* 1976).

The role of zinc alone or in combination with other substances in carcinogenesis is not clear. Certain zinc compounds administered by injection are carcinogenic, while others are not. In certain cases a zinc-supplemented diet, and in other cases a zinc-deficient diet, prevented or retarded the development of tumours (Furst 1977). Studying the enhancement of viral transformation of Syrian hamster embryo cells in *in vitro* tests for carcinogens and mutagens, $ZnCl_2$ and $ZnSO_4$ gave inconclusive results, but $ZnCrO_4$ showed a synergistic effect when compared with $CaCrO_4$ or K_2CrO_4 (Casto *et al.* 1979).

Increased levels of copper in serum albumin impaired the uptake of zinc by albumin. Increased dietary ratios of zinc to copper caused an increase in the serum cholesterol (Sandstead 1975).

A mutual antagonism between zinc and copper in the absorptive processes taking place in or on the intestinal epithelium has been reported by several workers (Underwood 1971; Fox *et al.* 1978).

Experiments with rats have shown that high levels of zinc placed directly into *in vivo* ligated segments of the rat gastrointestinal tract depressed the copper uptake but did not produce any change in the tissue distribution pattern (Van Campen 1966).

Zinc reversed the hypertension induced by cadmium (Masironi 1976), and preadministration of zinc counteracted the hypertensive effect of cadmium in rats (Perry and Erlanger 1975). The increased blood pressure in rats caused by the animals' drinking water which contained 2.5 mg Cd/L was prevented by a diet containing 22.3 mg Zn/kg and drinking water containing 100 mg Zn/L (Sandstead 1977).

The intraperitoneal administration of zinc to albino rats increased the liver uptake of cadmium administered by the same route. It was suggested that this effect was due to the stimulation of metallothionein synthesis by the administration of zinc; copper and mercury had similar effects (Shank and Vetter 1974; Parizek 1976). The intraperitoneal administration of zinc to guinea pigs (dose of 2.6 mg Zn/kg of body weight) doubled the urinary corticoid excretion. Doses of Ni^{2+} and Co^{2+} had the same effect; Hg^{2+} was lethal; and Cu^{2+}, Pb^{2+} and Fe^{2+} had insignificant effects (Sobel *et al.* 1960). A zinc-supplemented diet (15 to 120 mg/kg) reduced the cadmium absorption along the intestinal tract of Japanese quail (Jacobs *et al.* 1978).

Metabolic Interactions of Zinc with Other Substances

Zinc and calcium form an insoluble complex with phytate. In bone, increased calcium deposition is accompanied by increased zinc uptake by the bone. Increased calcium release from the bone, as in calcium deficiency, is accompanied by increased zinc release (Sandstead 1975).

In a study with rats which examined the interactions among zinc, lead, cadmium, calcium and vitamin D, it was found that the most severe growth depression occurred in animals fed high zinc (6300 mg Zn/kg of diet, as $ZnCO_3$) — low calcium (0.1% of diet) diets followed by high cadmium and high lead diets. Similarly, the most severe anemias occurred when high zinc and high lead (5000 mg Pb/kg of diet, as $PbCO_3$) were fed together. The addition of high zinc to a high lead diet appeared to reduce or block the excretion of urine ALA. A high zinc diet markedly reduced the lead concentration in blood, liver, kidney and bone (Willoughby and Thawley 1975).

A strong positive correlation was found between zinc and cadmium concentrations in samples of whole blood collected from children from Newark, N.J. The mean zinc concentration was 5.2 mg/L with values ranging from 1.5 to 17.3 mg/L (Bogden *et al.* 1974). An increase in the zinc concentration in the liver was observed after 30 to 35 weeks of dietary cadmium treatment of rats (100 mg Cd/kg of diet). All of the excess Zn^{2+} was located in the metallothionein. The increased zinc concentration in the liver was attributed to the increased synthesis of thionein induced by Cd^{2+} (Stonard and Webb 1976). An increase in the zinc concentration in the spleen of rats fed on a diet supplemented with cadmium was also reported by Julshamn *et al.* (1977). No change was observed in the zinc concentration of other tissues. The administration of a low dose of cadmium, 2.5 mg/L, in the drinking water of rats for 3 or 6 months did not change the concentration of zinc in the kidney or liver. The administration for a 12-month period slightly lowered the concentration of zinc in these two organs. Cadmium accumulated in the kidney, but not in the liver, after 3, 6 and 12-month experimental periods (Burgat-Sacaze *et al.* 1978). Results quoted by Sandstead (1977) showed that the ratio of cadmium:zinc is important in cadmium toxicity. Cadmium in drinking water was less toxic at a molar ratio of 1:4 than at a ratio of 1:1.

Simultaneous injection of zinc and cadmium to pregnant hamsters during early stages of gestation prevented the malformations in hamster embryos caused by cadmium alone. The administration of zinc 12 hours after the administration of cadmium failed to protect the embryos (Ferm and Carpenter 1968).

Pathological lesions were observed in the liver, lungs, heart and testes of rats fed on a low zinc diet and exposed to low doses of cadmium both orally and by inhalation. The kidney, usually the critical organ in cadmium exposure, did not show any morphological changes (Lal 1976).

Studies with rats have indicated that some of the symptoms caused by cadmium ingestion (e.g., decline in ceruloplasmin activity, reduction in the critical bone thickness in the femur) were exacerbated by a high intake of zinc (300 to 1000 mg/kg of diet) (Mills 1974).

Elinder and Piscator (1978) studied the accumulation of zinc and cadmium in the kidney and the liver of some laboratory and farm animals and man after long-term and low-level exposure to cadmium. They found significant differences between the various species and cautioned about extrapolation of data on zinc-cadmium relationships from laboratory animals to humans. For example, humans and large farm animals (lamb, pig, horse, bull, goat) showed equal or almost equal increases (in moles/kg) in the zinc

and cadmium concentrations in the renal cortex. The increase in the cadmium concentrations in the kidney of smaller animals (rabbit, rat, guinea pig, mouse, hen) was not accompanied by a similar increase in the zinc concentration. In liver, the Cd-Zn relationship seemed to be almost reversed, i.e., zinc concentration increased with cadmium concentration more markedly in smaller, laboratory animals than in larger animals.

Schrauzer *et al.* (1977) have correlated per capita dietary intake of several trace metals in 28 countries with age-corrected mortalities from various types of cancer. The zinc dietary intake had positive correlation coefficients greater than 0.5 with cancer of the intestine, breast, prostate, skin and blood (leukemia) (all Type A cancers). The strong association between the dietary intake of zinc with that of copper, cadmium and chromium precluded any definite conclusions. Zinc appears to stimulate tumour growth and is a selenium antagonist, possibly by lowering the physiological activity of selenium and by preventing selenium uptake. In the United States, an inverse correlation was observed between the blood levels of zinc and selenium. In large doses, zinc leads to symptoms of selenium deficiency. Experiments with mice have shown that zinc in the drinking water at a level of 200 mg/L cancelled the cancer-protecting effect of selenium (5 mg/L). Animals receiving only selenium had a significantly lower incidence of spontaneous mammary tumours. The incidence of breast cancer in several countries can be calculated with reasonable accuracy from the average dietary zinc and selenium intake or from their concentration in blood.

Zinc counteracted the lead suppression of ALA-D activity (Schlipköter *et al.* 1975). Intraperitoneal or dietary (0.6%) administration of zinc resulted in the reduction to near normal levels of urine δ-aminolevulinic acid (ALA-U) excretion and reticulocyte numbers in lead-intoxicated rats. This reduction was not accompanied by any significant reduction in the blood lead levels or any alleviation of the anemia of lead toxicity (Thawley *et al.* 1977, 1978). Rats which drank water containing 50 mg Zn/L and 100 mg Pb/L over a period of more than 4 months had lower lead concentrations in the tibia and the spleen than rats drinking water with the same lead concentration but containing only 5 mg Zn/L. The elevation of ALA-U, one of the symptoms of exposure to lead, was also lower in the group receiving the high zinc drinking water. Urinary excretion of lead, however, did not show any detectable changes due to zinc exposure (El-Gazzar *et al.* 1978). The lead levels in other organs and tissues (blood, brain, kidney, liver) were also almost the same in the two groups. The antagonism between lead and zinc was also shown in the lower zinc levels in plasma, liver and tibia of the animals exposed to lead. Zinc concentrations in the brain, kidney, testes and heart were not affected. Data quoted by Sandstead (1977) showed that rabbits exposed to tetraethyl lead lost 0.5 mole of zinc from the brain for every mole of zinc they retained.

Anemias produced by diets containing zinc (6300 mg/kg) or lead were more severe in rats fed diets low in calcium than in rats fed normal levels of calcium. When high levels of zinc and cadmium were fed together in low-calcium diets, a more severe anemic condition, as measured by the blood hemoglobin concentration, was observed than when either one was fed separately. A possible explanation is an increase in the gastrointestinal absorption of zinc, lead and cadmium associated with decreased intakes of calcium (Thawley *et al.* 1977).

Valentine and Chambers (1976) reported a significant positive correlation between zinc and lithium concentrations in samples of the water supplies and the age-corrected mortality from arteriosclerotic heart disease in the Houston (Texas) area. The zinc concentrations in the water samples ranged between 0.014 and 0.041 mg/L.

In experimental situations (golden hamsters), apparently zinc also had a protective effect against the teratogenic effects of mercury, presumably by inducing the production of metallothionein, which then complexed with mercury (Sandstead 1977).

Ingestion of ethylenediaminetetraacetic acid (EDTA) by female rats resulted in impaired reproduction and the congenital malformation of fetuses. These effects were prevented by the simultaneous administration of 1000 mg Zn/kg of diet (Swenerton and Hurley 1971). One side effect of the therapeutic use of EDTA is a marked increase, up to 20-fold, in the excretion of zinc. It is possible that the mucocutaneous lesions which appear in some cases of EDTA therapy are, at least in part, due to a zinc deficiency (Foreman 1963).

Pregnant rats maintained on a zinc-deficient diet (3 mg/kg) and receiving injections of EDTA showed a detectable increase in stress at parturition compared with rats subjected to zinc deprivation alone. The animals that received EDTA also showed a continuous loss of weight as would be expected after zinc depletion. None of these effects were observed in rats fed on a zinc-supplemented diet (100 mg/kg) and given the same EDTA dose (Apgar 1977).

Dermal application of fenitrothion changed the distribution of zinc (also Cu and Mn) in various organs of adult male albino rats. The zinc concentrations on a fresh weight basis increased in the kidney, spleen, brain, heart and plasma (Khanna *et al.* 1975).

Diets containing 200 mg Zn/kg (as $ZnSO_4$) or oral doses of $ZnSO_4$ prevented or increased the resistance to sporidesmin poisoning in rats. Sporidesmin is the major toxin in *Pithomyces chartarum*, the cause of an economically important mycotoxicosis in New Zealand characterized by liver damage in sheep and cattle that graze on pasture contaminated by this fungus (Towers 1977).

Recommended Limit for Zinc Concentration in Raw Public Water Supplies

Zinc is one of the essential elements of life and it is widely available through a normal, well-balanced diet. Such a diet supplies approximately 10 to 20 mg Zn/d. The drinking water generally supplies only a small fraction of the daily intake. In the United States it was estimated that the median zinc intake via the drinking water was 0.5 mg/d, the maximum intake being 2.1 mg/d. The zinc intake via food was estimated at 13 mg/d (Schroeder 1974b). The relatively low contribution of the drinking water to the total dietary zinc intake is probably the reason why the zinc levels in the drinking water could not be correlated with the zinc concentrations in various body tissues or fluids (Sharrett 1977).

Zinc deficiency produces a series of undesirable symptoms. Zinc can also be toxic and accumulate in certain tissues but only at very high dietary concentrations and very high intake rates.

In a survey of drinking water carried out across the United States, zinc was found in all samples and the average concentration was 0.194 mg/L (Craun and McCabe 1975). Concentrations of up to 3.756 mg Zn/L were found in tapwater samples from four areas of the eastern United States (Strain *et al.* 1975). Zinc concentrations in rural potable water (Hampton County, South Carolina) ranged between 0.01 and 2.18 mg/L with an average of 0.354 mg/L (Sandhu *et al.* 1978). A national survey conducted in Canada found a median value of $\leqslant$0.005 mg Zn/L and a range of $\leqslant$0.005 to 0.200 mg/L in treated and distributed drinking waters (Méranger *et al.* 1979). For comparison, in raw water the median value was the same, while the range went up to 0.330 mg/L.

Treatment of water for removal of zinc does not seem to be a problem. Weston and Morrell (1977) quoted data which showed that even with simple treatment, i.e., lime precipitation and clarification, zinc concentrations of around 1 mg/L were achieved. When filtration was added, concentrations of 0.1 to 0.4 mg/L were obtained. In a survey of 12 conventional (clarifiers and filters) water treatment plants Zemansky (1974) found that the zinc removal ranged from 0% to 90%. Conventional biological treatment removed 35% to 80% of the zinc from wastewaters. A ferric chloride-activated carbon treatment removed 94% of the zinc (influent concentration 5.0 mg/L). At a wastewater treatment plant in Dallas (Texas) activated sludge removed 65% of the influent zinc concentration of 0.320 mg/L. When the activated sludge treatment was followed by lime (pH 11.5), filtration and activated carbon treatments, the zinc removal reached 91% (Cohen 1977). Sewage treatment plants in Ontario removed 57% to 74% of the influent zinc (average 60%) (Atkins and Hawley 1978, p. xi).

Both the Environmental Protection Agency in the United States and the Australian water quality criteria recommend a zinc concentration of 5 mg/L in domestic water supplies (EPA 1976; Hart 1974, p. 60). The same limit was also recommended by the World Health Organization (WHO 1971). In Canada the federal-provincial working group on drinking water also recommended a maximum concentration of 5 mg Zn/L in the drinking water based on aesthetic and taste considerations (HWC 1979).

Since zinc is an essential element of life, it offers some protection against the toxic effects of other metals, and unless it reaches very high concentrations, probably above 1000 mg/L, it is not toxic. A maximum concentration of 5 mg/L is recommended for raw public water supplies. Concentrations of up to 10 mg/L can be allowed in waters that will be treated before entering the distribution system. As mentioned in the section of "Natural distribution of zinc," the surface waters in Canada do not reach these concentrations.

Aquatic Life

Levels of Zinc in Fish

As mentioned in the section on "Zinc in the human body and laboratory animals," zinc is an essential element for animals and plants. It is a structural metal in many enzymes and is essential for their activity. Zinc is necessary for growth, reproduction and the formation of RNA and DNA (IJC 1976; Luckey *et al.* 1975). Its deficiency alters the metabolism of RNA, DNA and proteins, and the cellular balances of other elements, including magnesium, manganese and iron (Falchuk *et al.* 1977; Riordan 1976).

The concentration of zinc in fish has been studied by a number of researchers. The range of zinc in the liver of Great Lakes fish at least 2 years old ranged from 11 to 48 mg/kg (wet weight) (Lucas *et al.* 1970). Mean levels of zinc in whole fish caught in Lake Huron offshore waters ranged from 11.8 to 17.2 mg/kg (Armstrong and Lutz 1977). The concentrations of zinc in composite

dressed samples of fish from Lake Erie ranged from 11 mg/kg in northern pike to 20 mg/kg in rainbow smelt. Lake whitefish from Lake Ontario and yellow perch from Lake Erie contained 12 mg Zn/kg (Uthe and Bligh 1971). Concentrations of zinc in muscles of fish caught in Toronto Harbour were higher than in fish from Baie du Doré (Lake Huron). Muscle, liver and kidney mean concentrations from Toronto Harbour fish were 36.02, 89.04 and 59.41 mg/kg wet weight compared with concentrations in Baie du Doré fish of 4.69, 15.10 and 26.09 mg/kg, respectively, reflecting the more polluted state of Toronto Harbour (Brown and Chow 1977).

Zinc was present in detectable quantities in nearly all the fish sampled from the lower Fraser River, B.C. The concentration varied between the different fish species. Zinc levels were highest in northern squawfish, peamouth chub and prickly sculpin (maximum 21.01 mg/kg). The concentrations were dependent on the size of the fish, decreasing in larger fish (Northcote *et al.* 1975).

Fish inhabiting lakes in the Northwest Territories affected by gold and silver-copper mine wastes contained higher levels of heavy metals than fish from other lakes and rivers in the same area. Sediments also contained high levels well in excess of background. Zinc accumulated in the liver 4- to 8-fold more than in muscle. The highest liver concentrations in Baker Creek fish were in northern pike (60.5 mg/kg) and whitefish (52.7 mg/kg). Fish from rivers draining areas rich in metal ores also contained high levels. The liver of whitefish and northern pike from Ho-Hum Lake, a tailings pond, contained 55.6 and 120.4 mg/kg, respectively. The fish appeared to be healthy, but females were either barren or contained fewer and smaller eggs than fish from less contaminated areas (Falk *et al.* 1973).

The levels found in muscles in the above studies were much less than the Canadian standard for human consumption of 100 mg/kg (wet weight) (NHW 1976).

Bioaccumulation of Zinc by Aquatic Organisms

Rabe and Bauer (1977) showed that the accumulation of zinc by aquatic organisms depended on the trophic states. Zinc concentrations were greater in benthic insects than in fish, and higher in omnivorous fish than in piscivorous species. Zinc concentrations in the muscle of five species of fish varied from 19.5 mg/kg in largemouth bass to 67.6 mg/kg (dry weight) in brown bullheads. Liver concentrations ranged from 107.2 mg/kg in the pumpkinseed to 120.5 mg/kg in largemouth bass to 232.1 mg/kg in the brown bullhead. Dissolved zinc concentrations in the water ranged from 0.05 mg/L in open water to 0.44 mg/L nearer the inlets to some of the lakes in the study system, to 1.1 mg/L in the Coeur d'Alene River. Zinc levels in sediments also varied (240 to 5200 mg/kg) depending on distance from contamination sources; the values were higher in sediments of lakes closer to mining waste discharges. The zinc content of chironomids (midges) decreased with distance from the more contaminated areas. Midges contained 858 mg/kg (dry weight) from an area with 3250 mg Zn/kg in the sediment. A predaceous dragonfly nymph (*Cordulia* sp., Libellulidae) contained lower concentrations of zinc (185 mg/kg) than omnivorous forms.

The distribution of zinc in a pond system showed a mean of 0.016 mg/L in the water, 477 mg/kg in the net plankton and 410 mg/kg in the benthos. Omnivorous fish contained more zinc (313 mg/kg) than carnivorous fish (18.6 and 265.1 mg/kg). The top layer (3 cm) of sediment contained more zinc, 219.6 mg/kg, than lower levels, reflecting the nearness of the pond to an urban community, which was the source of the pollutants (Namminga *et al.* 1974).

The distribution of zinc through a river system in Illinois affected by industrial effluents showed that high concentrations of zinc were present in the sediments and that benthic organisms contained more zinc than the fish. The water contained the lowest concentration (0.031 mg/L). The mean level of zinc in the sediments was 81 mg/kg and ranged from 41 to 95 mg/kg in the benthic organisms. Omnivorous fish muscle had higher levels of zinc (means of 2.6 to 10.2 mg/kg) than carnivorous fish (means of 2.6 to 4.5 mg/kg) (Mathis and Cummings 1973).

The concentration factors (ratio of zinc concentration in alga to the concentration in filtered water) for *Cladophora glomerata* from Lake Ontario were 2900 (metal content of alga, 23.7 mg Zn/kg) and 1000 (8.2 mg Zn/kg) for a part of the lake near Kingston and an isolated part of the lake, respectively (Keeney *et al.* 1976). Zinc concentrations in algae reflected the concentration of zinc in the water. Waters adjacent to zinc smelting waste tips had a mean zinc concentration of 16.78 mg/L, and algae growing in the water had a concentration of 26 570 mg/kg. Corresponding zinc concentrations for sites distant from the smelter were 0.12 mg/L and 980 mg/kg. The dominant species in the two waters differed. Those near the smelter were *Coccomyxa*, *Tribonema*, *Mougeotia* and *Zygnema*; those in distant waters were *Cladophora*, *Spirogyra* and *Oedogonium*, showing differences in species sensitivity to zinc and the other metals present in the wastes (Trollope and Evans 1976).

Zinc concentrations in *Chlorella* (alga) reached a maximum after five generations. The development of resistance to zinc appeared to be related to a zinc exclusion

phenomenon. There was a marked reduction of zinc-65 uptake by resistant cultures and a lower number of sites in the cell walls were available for zinc ions. The zinc exclusion was primarily governed by an inhibition of the active component of zinc uptake (de Filippis and Pallaghy 1976).

Up to 40% of the zinc associated with submerged macrophytes was contained in epiphytes. This would be of importance when considering the intake of heavy metals by organisms grazing on the surface of the plants. When epiphytes were removed, the amount of zinc in macrophytes with roots and the metabolic activity of the plant appeared to be correlated with the amount of zinc in the sediment (Patrick and Loutit 1977).

Aquatic mosses had higher concentration factors (av. 9400 and 2500) than flowering aquatic plants (av. 165 and 2000) (Dietz 1973).

Solbé (1977) indicated that macroinvertebrates and fish were adversely affected by a steel works effluent entering a stream which had its source in the neighbouring limestone hills. The observed concentration of dissolved zinc (passing through a 0.45 μm pore membrane filter) in the river was 25 mg/L. Ammonia, the only other pollutant found at concentrations toxic to aquatic life, was quickly oxidized. McLean and Jones (1975) studied the distribution of flora in two rivers affected by old lead mines. Some species of moss and algae were relatively resistant to zinc and contained quite high levels of the metal. Stream levels of total zinc ranged from non-detectable to 21.84 mg/L, and soluble zinc from non-detectable to 15.35 mg/L. Plants accumulated zinc from the water. For example, *Scapania undulata*, a tolerant moss growing in water containing 1.2 mg Zn/L, had a zinc concentration of 1950 mg/kg.

Bacteria from sediments contaminated by sublethal mixtures of heavy metals (2 mg/L of each metal Zn, Cr, Cu, Mn, Fe, Pb) in the culture medium absorbed 1127 mg Zn/kg (dry weight) after incubation for 7 days at 28°C. With no zinc added, the bacteria absorbed 528 mg Zn/kg. The bacteria in turn were ingested by worms (*Tubifex* sp. and *Limnodrilus* sp., Tubificidae) which accumulated 868 mg Zn/kg (dry weight) compared with worms fed bacteria cultured in the absence of heavy metals and which had a zinc concentration of only 262 mg/kg. The tubificids were left in doubly distilled water overnight to allow them to discharge gut contents so that only absorbed zinc was measured (Patrick and Loutit 1976).

The distribution of chironomids was affected by the concentrations of heavy metals in the sediments of a lake receiving effluent from an electroplating plant and containing Zn, Cr and Cd. *Chironomus tentans* was absent from the most highly contaminated areas (14 032 mg Zn/kg), but *Limnodrilus* sp. (oligochaete-worm) was abundant; no explanation for the seemingly high tolerance to zinc was given. The chironomid was abundant in areas where the sediment had a lower degree of contamination, 139 to 5587 mg Zn/kg (Wentsel *et al.* 1977a). Laboratory bioassays were conducted to determine the percentage of chironomids surviving in the contaminated sediments. Only 47.5% of the chironomids from the uncontaminated end of the lake survived exposure to contaminated sediments (15 100 mg/kg), but 75% of those (in the laboratory experiments) from the contaminated end survived exposure to the sediments. This difference was significant and indicated that the chironomids from the contaminated end were more resistant to heavy metal contamination. The chironomids from the uncontaminated end had a higher avoidance response to contaminated sediments (8280 mg Zn/kg) than those from the contaminated part of the lake (Wentsel *et al.* 1978).

The uptake of zinc-65 by chironomid larvae was inhibited by the presence of cadmium in the water. The concentration factors (concentration in chironomid/concentration in water) of zinc were 87, 167 and 157 in the presence of 0.02, 0.01 mg/L and no cadmium, respectively (Berg and Weiss 1975). Mayflies (Ephemeroptera) and stoneflies (Plecoptera) had concentration factors (C.F.) ranging from 257 to 2990 and 41 to 571, respectively (Nehring 1976). The uptake of zinc by fish did not appear to be influenced by the presence of cadmium and vice versa (Spehar *et al.* 1978), in contrast with uptake by the aquatic plants *Lemna* and *Salvinia* (Hutchinson and Czyrska 1975). Zinc inhibited the uptake of the radionuclide strontium by fish (Berg and Merlini 1972).

Goldfish (*Carassius auratus*) and catfish (*Corydores aeneus*), both bottom feeders, were exposed to zinc-contaminated sediments for 5 months. The maximum amount of metal was accumulated in 2 months, followed by a slight decline and then a small increase. The total zinc in the sediment was 40 500 mg/kg, decreasing to 18 200 mg/kg at the end of 5 months. Part of the zinc was lost with the fine sediments on the test apparatus filter system. The peak accumulation of zinc in goldfish was 450 mg/kg (wet weight) and 125 mg/kg in catfish. A midwater feeder, the zebra fish (*Brachydanio rerio*) accumulated between 2.4 and 10 times less zinc than the bottom feeders and indicated the role of sediment and feeding habits in heavy metal accumulation by fish (Delisle *et al.* 1975).

Concern has been expressed about the accidental release of radionuclides into the environment. A study by Brungs (1967) showed that there was an initial rapid loss of dissolved zinc-65 from the water and only about 6% of

it remained in solution after day 4, a large fraction being sorbed onto suspended materials, where after 2 days, the concentration was 2 or 3 times greater than that in solution. Zinc-65, as is found with most metals, was more associated with the fine sediments than with the coarse. Primary consumers, such as snails, clams and carp, accumulated more zinc-65 than the bluegill (macroinvertebrates, fish fry, small amount of algae). The rate of accumulation was gradual in bluegills but was initially more rapid in clams, tadpoles and snails. Berg and Weiss (1975) also documented a gradual accumulation of zinc-65 by fish. Watson *et al.* (1969) reported on the movement of a number of radionuclides through the ecosystem during and after a shutdown at the Hanford reactor on the Columbia River. There was a rapid and extensive decline in the concentration of radionuclides in the biota, particularly in forms such as periphyton where adsorption is thought to play a major role in metal uptake. There were slower rates of uptake and loss of zinc-65 by fish. The half-life of zinc-65 for periphyton was 15 hours and for fish, 134 days. There was evidence for heavy metal recycling from the sediments to the biota during reactor shutdown.

Gills and liver of sticklebacks (*Gasterosteus aculeatus*) accumulated the most zinc, with concentration factors of 5.1 and 3.8, respectively, at 16 hours with respect to the surrounding water, which contained 1 mg Zn/L. The lowest concentration was in the gonads (C.F. 0.8). On a logarithmic scale there was a positive linear relationship between the zinc uptake from water and the wet weight of fish. However, the larger fish absorbed less Zn-65 per gram of tissue. There was strong evidence that the main route of uptake was through the gills, as zinc and oxygen uptake rates were very similar. A state of equilibrium with the water was reached at different times depending on the species of fish. When fish were placed in zinc-free water, the amount of zinc they lost also depended on the species of fish and loss seemed to be facilitated by the presence of calcium ions. It was also demonstrated that fish in high calcium water could withstand more absorbed zinc and remain healthy than fish in low calcium. The fish in low calcium water exhibited symptoms of acute zinc poisoning (Matthiessen and Brafield 1977).

Tissue analysis of brook trout exposed to zinc indicated that the greatest accumulation was in the gill, kidney and opercular bone. The amount of zinc per whole tissue taken up by second-generation trout tended to be fairly stable between 52 and 93 weeks except for slight increases in the zinc content of liver and kidney tissues of fish exposed to 0.534 mg Zn/L. This apparent steady state could be explained by the presence of homeostatic control mechanisms. After the fish were transferred to clean water, the accumulation of zinc in the kidney continued and the zinc was probably translocated from other parts of the body. Gills, liver, kidney and opercular bone dissected from trout exposed to 1.38 mg Zn/L for 20 weeks contained 4.8, 2.9, 1.6 and 5.4 times more zinc, respectively, than similar tissues from control fish. Spleen, muscle and gonad tissues did not accumulate any significant residues in the 20 weeks (Holcombe *et al.* 1979).

Zinc accumulated with age in flagfish, but the accumulation rate was slower than the growth rate. The amount of zinc taken up by the fish increased with increasing exposure concentration; approximately 200 and 300 mg/kg accumulated in fish exposed to 0.08 and 0.14 mg Zn/L, respectively, for 30 days (Spehar 1976).

Temperature affected the rate of zinc uptake, and this accelerated with time and temperature. Warm acclimated fish died faster as zinc was taken up more rapidly to reach a lethal concentration and not because the fish were more sensitive to zinc than cold acclimated fish. Gills from fish acclimated at 19°C had significantly more zinc-65 than gills from fish acclimated at 11°C and 3°C (Hodson 1975).

Observations on the Effects of Zinc under Natural Conditions

Smelters at Flin Flon (Manitoba) processing a copper, zinc, silver and gold sulphide ore caused heavy concentrations of zinc and other heavy metals to accumulate in lakes in the area. In a study of 31 lakes, 7 had average zinc concentrations above 0.1 mg/L, 6 had levels between 0.05 and 0.1 mg/L and the rest had concentrations of <0.05 mg/L. The main source of the heavy metals for many of the lakes was atmospheric fallout. Two lakes receiving effluent from the smelters had zinc concentrations of 1.3 and 8 mg/L. Fish in lakes containing up to 0.09 mg Zn/L and approximately 0.01 mg Cu/L did not show noticeable adverse effects from the metals, but long-term effects may not yet have been detectable. In some of the lakes with higher levels of zinc, some species of fish were more affected than others. For example, catches of white sucker, walleye and lake whitefish were greatly reduced, and the spawning of white sucker appeared to be partially impaired. Laboratory studies have shown harmful effects of zinc or zinc-metal mixtures on fish and other aquatic organisms to occur over the range of about 0.030 to 0.200 mg Zn/L. In the field many extraneous factors could affect toxicity (Van Loon and Beamish 1977).

McFarlane and Franzin (1978) studied the effects of heavy metal fallout on white sucker (*Catostomus commersoni*) populations in two chemically and physically similar lakes near Flin Flon, Manitoba. Analysis of the age of the fish suggested that longevity was reduced in Hamell (sic)

Lake, which was more severely affected by heavy metals. In Hamell Lake, mean concentrations over 1 year in filtered water were Cu, 0.013; Cd, 0.0006; and Zn, 0.211 mg/L; and in Thompson Lake, they were Cu, 0.014; Cd, 0.0001; and Zn, 0.014 mg/L. The growth rate and fecundity (the capacity of fish to produce reproductive units) of white suckers in Hamell Lake was higher than in Thompson Lake, but the mean egg diameter was significantly smaller in Hamell Lake fish. The females matured earlier in Hamell Lake (av. 3 to 4 years) than in Thompson Lake (5 to 7 years). Most of the females caught in Thompson Lake were spent (eggs were shed), but very few in Hamell Lake had spawned and the eggs were being resorbed. Fewer fish per unit effort (number of fish caught divided by the product of the number of square metres of fish net used and the number of hours fished) were caught in Hamell Lake. Populations were normally distributed for age and sex and the older fish in both lakes had similar mortality rates, but there was a high mortality either prenatally or for early larval stages in Hamell Lake. A random sample would suggest that the white sucker populations were healthy and thriving, but comparing the catch per unit effort, the spawning success, egg size and longevity, it was suggested that the Hamell Lake population was under stress. Heavy metals were elevated in Hamell Lake and zinc was particularly so in the spring. The reduced reproductive success was probably due to the high cadmium and zinc levels. Fish respond to severe stressing of the young stages by compensatory increased fecundity and this was observed in the Hamell Lake population. Walleye and lake whitefish populations have declined in Hamell Lake since 1973, which corresponded with an increase in heavy metals in the lake for this period.

The Northwest Miramichi (New Brunswick) contains salmon runs, and Sprague and Saunders (1963) conducted studies which illustrated that copper and zinc in the river affected fish movement, and that if concentrations were high enough, the metals could block or partially block spawning migration. The downstream movement of fish, totalling 22% of the fish that had previously gone upstream, seemed to occur when pollution exceeded about 0.425 ILL (incipient lethal level) of copper and zinc (mixture) in the river water in 1962 and 0.35 ILL in 1961. Only 1% to 2% of the fish returned downstream when no mining was taking place. Tests with caged fish showed that levels of copper and zinc could reach lethal levels in the river.

Differences between the length and weight of midge larvae inhabiting two parts of a lake, one area contaminated by zinc (16 400 mg Zn/kg sediment) and the other uncontaminated (77 mg Zn/kg sediment), illustrated sublethal effects of zinc on an aquatic organism in its natural environment. The zinc had significantly adverse effects on the growth of the midge. The mean lengths were 0.82 and 1.83 cm, and the mean weights 0.2 and 2.86 mg for midges from contaminated and uncontaminated areas, respectively (Wentsel *et al.* 1977b).

Harding and Whitton (1976) studied *Stigeoclonium tenue* (alga) from 34 different sites, the majority of them being affected by past or present mining activities. Absolute values for toxicity in the laboratory were almost always higher (i.e., a lower concentration was more toxic in the laboratory) than those obtained in the field where other environmental factors were present, making it difficult to compare field and laboratory situations. The results of toxicity tests showed that populations of *S. tenue* growing in zinc-polluted streams were genetically adapted forms able to withstand higher concentrations of zinc than populations from unpolluted streams. The highest zinc level at which *S. tenue* was found in England was 7.1 mg/L, though the same species was found in a German river with 20 mg Zn/L. Analysis of the mean field zinc levels and *S. tenue* resistance indicated that the alga was more resistant to zinc from sites with zinc concentrations of 0.2 mg/L or more. McLean (1974) showed that *Stigeoclonium tenue* was found in rivers containing up to 0.53 mg Zn/L but was absent from rivers with higher levels. Higher tolerances have been reported by other authors, but it was suggested that conditions for growth were not at a maximum in the study area used by McLean, hence the lower tolerances.

Differences in the tolerance of algae to zinc depending on the zinc content of the river were also found by Say *et al.* (1977). The filamentous alga *Hormidium rivulare* from a river (pH 6.6, total hardness 21 mg/L as $CaCO_3$) containing 0.02 mg Zn/L was killed by 1.92 mg Zn/L. The level of zinc just non-inhibitory to growth was 1.14 mg/L. *H. rivulare* from a river (pH 6.8, total hardness 53.2 mg/L as $CaCO_3$) containing 1.52 mg Zn/L was killed by 23.5 mg Zn/L but was not affected by 10.6 mg Zn/L.

The Effects of pH, Hardness, Alkalinity, Temperature and Dissolved Oxygen on Zinc Toxicity

Hardness, Alkalinity and pH

A good discussion on the effects of these variables on zinc toxicity is given in Spear (1980, in press). A few points are discussed in the following section.

Algae—Magnesium and calcium, which are hardness factors, decreased the toxicity of zinc to algae (Say and Whitton 1977). A decrease in pH was shown to decrease the toxicity of zinc to *Hormidium rivulare*, an acid stream species of filamentous alga (Hargreaves and Whitton 1976; Say and Whitton 1977). In contrast, for a zinc-tolerant

population of *Stigeoclonium tenue*, an increase in pH from 6.6 to 7.6 decreased the toxicity of zinc to the alga. An increase in hardness also decreased the toxicity, but to a lesser extent, for a zinc-sensitive population (Harding and Whitton 1977).

Fish—As with algae, pH had an effect on the toxicity of zinc to fish. An increase in pH from 6 to 8 was accompanied by an increase in toxicity, and an increase in hardness decreased the toxicity of zinc (Pagenkopf 1976). In contrast with other studies, an increase in pH decreased the toxicity of zinc to bluegill sunfish (Cairns *et al.* 1971). These tests were static and this enabled the zinc, precipitated out at the higher pH, to settle and not affect the fish.

Holcombe and Andrew (1978) demonstrated that there was an increase in zinc toxicity with increasing pH and a decrease with increasing hardness to two species of trout. By increasing the water hardness from 44 to 170 mg/L (as $CaCO_3$) and maintaining a constant alkalinity, the toxicity of zinc was decreased by a factor of 2.5 and 2.1 for rainbow and brook trout, respectively. Increasing both hardness (from 47 to 179 mg/L, as $CaCO_3$) and alkalinity (from 42 to 170 mg/L, as $CaCO_3$) decreased zinc toxicity by a factor of 5.7 to 6.8 and 3.3 to 3.9 for rainbow and brook trout, respectively. LC_{50}'s for both rainbow and brook trout were positively correlated with the hardness and alkalinity (correlation coefficients of 0.85 to 0.96) and negatively with the pH (correlation coefficient of -0.83). The actual regression equations of LC_{50}'s vs. hardness, alkalinity and pH showed that of these three independent variables, a change in pH most affected the LC_{50} for both rainbow and brook trout. At a constant hardness and alkalinity, the LC_{50} for trout varied by a factor of approximately 2 for each unit change in pH. The means for the actual LC_{50}'s measured in soft water (hardness approximately 46 mg/L, as $CaCO_3$) and in different conditions of alkalinity and pH ranged from 0.370 to 0.756 mg Zn/L for rainbow trout, and from 1.55 to 2.42 mg Zn/L for brook trout. In hard water (hardness of approximately 175 mg/L, as $CaCO_3$) the range of mean LC_{50}'s for rainbow trout was 1.91 to 2.96 mg Zn/L, and for brook trout 4.98 to 6.98 mg Zn/L.

Mount (1966) studied the relationship between zinc toxicity and different pH and hardness values using fathead minnows. At any given hardness, zinc was more toxic at a high pH (8) than at low pH (6). For example, at pH 6 and hardness 50 mg/L as $CaCO_3$, the LC_{50}'s based on measured Zn^{2+} were 12.5 and 13.8 mg Zn/L, and at pH 8, 4.7 and 5.1 mg/L. At pH 6 and hardness 200 mg/L as $CaCO_3$, the LC_{50}'s were 29.0 and 35.5 mg Zn/L, and at pH 8, 8.2 and 15.5 mg Zn/L. Death at pH 8 was related to visible precipitation of zinc salts and an accumulation of zinc precipitate was observed between the gill filaments. There was also a much greater sloughing of mucus in the higher pH tests. Analysis of the water at pH 8 and hardness 200 mg/L as $CaCO_3$ showed substantially less zinc in solution after filtration through a 0.45 μm membrane filter. A greater effect of an increase in hardness was present between 50 and 100 mg/L as $CaCO_3$ than between 100 and 200 mg/L as $CaCO_3$. The author suggested that further work on the effects of pH is needed. The gills of fish from all test combinations of pH and hardness showed evidence of epithelial breakdown.

The acute toxicity of zinc, besides being affected by the quality of the water, also varied from species to species (Table 3). Caution must be applied when discussing and using experimental results done at different times and locations for setting water quality objectives, especially when local water conditions are very different from the experimental conditions. The size of the fish appeared to have an effect on the sensitivity of rainbow trout. The 96-h LC_{50} for fish 70 mm and 140 mm long was 0.24 and 0.56 mg/L, respectively, in soft water (22 and 23 mg/L as $CaCO_3$). In very hard water (312 mg/L as $CaCO_3$) the corresponding concentrations of zinc were 1.19 and 4.52 mg/L, respectively. In water of 102 mg/L hardness, fish 190 mm long had a 96-h LC_{50} of 1.0 mg Zn/L. As can be seen from Table 3, the acute toxicity for four species of trout varied quite widely (Goetti *et al.* 1976?). The 48-h LC_{50} for rainbow trout in hard water (240 mg/L as $CaCO_3$) was 4 mg/L (Brown and Dalton 1970).

The effect of hardness on the toxicity of zinc, using waters with a hardness of 330 mg/L and 25 mg/L as $CaCO_3$ and rainbow trout (*Salmo gairdneri*), was studied by Sinley *et al.* (1974). The 96-h LC_{50} values for juvenile trout in hard and soft water at 15°C were 7.21 and 0.43 mg Zn/L. The LC_{50} for eyed eggs was 2.72 mg/L in soft water. In chronic studies, the MATC, maximum acceptable toxicant concentration (using mortality of fry), was between 0.32 and 0.64 mg/L in hard water (hardness of 330 mg/L as $CaCO_3$), and 0.14 and 0.26 mg/L in soft water (hardness of 25 mg/L as $CaCO_3$). There were no differences between the growth rates of fish at any of the zinc concentrations tested.

Temperature

A rise in the temperature of the test water increased the toxicity and decreased the time to death for the same zinc concentration (Water Research Centre 1967). Bluegills acclimated to 20°C and 30°C and then exposed to a lethal concentration of zinc (32 mg/L) at each temperature died 2.6 times faster at 30°C than at 20°C. Fish acclimated to

Table 3. Some Acute Toxicities of Zinc to Different Species of Fish

Species	Water hardness, mg/L as $CaCO_3$	96-h LC_{50} mg Zn/L	Reference
Phoxinus phoxinus (minnow)	64	3.2±0.5	Bengtsson 1974b
Pimephales promelas (fathead minnow)	20	0.78 to 0.96	Pickering and Henderson 1966
Pimephales promelas (fathead minnow)	360	33.4	Pickering and Henderson 1966
Pimephales promelas (fathead minnow)	200	9.2	Brungs 1969
Lepomis macrochirus (bluegill)	20	0.489 to 0.58	Pickering and Henderson 1966
Lepomis macrochirus (bluegill)	360	40.9	Pickering and Henderson 1966
Lebistes reticulatus (guppy)	20	1.27	Pickering and Henderson 1966
Salmo gairdneri (rainbow trout)	15	0.57	Sprague 1968a
Salmo gairdneri (rainbow trout) (70 mm length)	22	0.24	Goettl *et al.* 1976?
Salmo gairdneri (rainbow trout) (140 mm length)	22	0.56	Goettl *et al.* 1976?
Salmo gairdneri (rainbow trout) (70 mm length)	312	1.19	Goettl *et al.* 1976?
Salmo gairdneri (rainbow trout) (140 mm length)	312	4.52	Goettl *et al.* 1976?
Salmo gairdneri (rainbow trout) (190 mm length)	102	1.0	Goettl *et al.* 1976?
Salmo gairdneri (rainbow trout)	32 to 54	0.41	Goettl *et al.* 1976?
Salmo gairdneri (rainbow trout)	25	0.43	Sinley *et al.* 1974
Salmo gairdneri (rainbow trout)	330	7.21	Sinley *et al.* 1974
Salmo clarki (cutthroat trout)	32 to 54	0.67	Goettl *et al.* 1976?
Salmo trutta (brown trout)	32 to 54	0.64	Goettl *et al.* 1976?
Salvelinus fontinalis (brook trout)	32 to 54	0.96	Goettl *et al.* 1976?

20°C and exposed and tested at temperature increases of 1.5°C every 10 minutes to a maximum of 30°C died 4.8 times faster than fish maintained and tested at 20°C. A sublethal concentration of 0.056 mg Zn/L produced no mortalities in 20°C-acclimated bluegills in 96 hours but was toxic when the temperature was increased from 20°C to 30°C at a rate of 1.5°C every 10 minutes (Burton *et al.* 1972b). Temperature effects would be of concern in lakes or rivers receiving industrial effluents.

Atlantic salmon exposed to zinc at acclimation temperatures of 3°C, 11°C and 19°C had toxicity curves (Zn concentration vs. time to death) with the same shape. The fish were more tolerant at the lower temperature. If temperature stress (the application of a rapid increase or decrease in temperature) was present, the slope of the toxicity curves changed and zinc toxicity was enhanced. Fish acclimated to 3°C had a shorter survival time when exposed to a heat stress in the presence of zinc than the fish acclimated at the higher temperatures, indicating that the cold-acclimated fish were less tolerant (Hodson and Sprague 1975).

Hodson (1976) discounted the hypothesis that the higher lethal threshold to zinc toxicity of warm-acclimated fish, compared with that of cold-acclimated fish (rainbow trout), was due to an increased resistance to tissue hypoxia (induced by gill damage). Lactic acid is a product of hypoxic tissue metabolism and it was shown that relative lactic acid concentrations did not increase with an increase in temperature, but did increase significantly with time and zinc exposure. The increases in lactic acid concentrations were the same at the three test temperatures of 3°C, 11°C and 19°C.

Dissolved Oxygen

Blood pH and gaseous exchange are partly controlled by the zinc-containing enzyme carbonic anhydrase, which has been found in the red blood cells, gills and kidneys of fish. Inhibition of this enzyme causes similar symptoms to those found in fish exposed to zinc (Hoffert and Fromm 1968). *In vitro* studies have shown that metabolically active tissues cannot utilize oxygen, even if there is an adequate supply, when an excess of zinc ions are present (Hiltibran 1971). Zinc toxicity seems to interrupt gaseous exchange both at the tissue level and because of damaged gill epithelia.

Low dissolved oxygen levels increased the toxicity of zinc to the bluegill. The 20-d LC_{50}'s at 1.8, 3.2 and 5.6 mg O_2/L were 7.2 to 7.5, 10.5 to 10.7 and 10.7 to 12.0 mg Zn/L, respectively, in water with a hardness of 370 mg/L as $CaCO_3$ (Pickering 1988). Thus, conditions with low dissolved oxygen must be taken into consideration when establishing a water quality objective for zinc.

Additional Acute Toxicity Studies

Toxicity to Fish Eggs

Eggs of the fathead minnow became more fragile on exposure to zinc (Brungs 1969; Benoit and Holcombe 1978). This increase in fragility would affect the egg survival of species that use gravel spawning beds. It was indicated that zinc interfered with the water-hardening process of the outer egg membrane; zinc (Zn^{2+}) may compete with calcium (Ca^{2+}) during the egg-hardening process. The variation of the calcium ion concentration of the water varied the degree of hardening attained in brook trout eggs (Hurley and Fisher 1966). The effect of zinc on the outer membrane strength was lessened after the eggs were water hardened (Holcombe *et al.* 1979).

Pickering and Vigor (1965) studied the acute toxicity of zinc to eggs and fry of the fathead minnow. The 96-h LC_{50} for eggs was 1.85 and 1.82 mg Zn/L and the 12-d LC_{50} was 1.57 and 1.69 mg Zn/L (duplicate tests, water hardness 174 to 198 mg/L as $CaCO_3$). The 96-h LC_{50} for fry was 0.87 mg/L, the fry being more sensitive than the eggs.

Insects

Mayflies and stoneflies (Insecta) were found to be more tolerant to zinc than fish. The 14-d LC_{50}'s for *Ephemerella grandis* (mayfly) and *Pteronarcys californica* (stonefly) were >9.2 and >13.9 mg Zn/L, respectively, in water of hardness 30 to 70 mg/L as $CaCO_3$ (Nehring 1976).

Other Invertebrates

Invertebrates vary widely in their susceptibility to zinc. Four species of snail were shown to have sensitivities similar to some algae. The 48-h LC_{50}'s for *Physa integra*, *Goniobasis livescens*, *Lymnaea emarginata* and *Helisoma anceps* were 4.4, 7.7, 4.15 and 5.2 mg/L, respectively (hardness of 136 to 171 mg/L (Cairns and Messenger 1974). The 96-h LC_{50} for *Physa heterostropha* was 0.79 to 1.27 mg Zn/L (Patrick *et al.* 1968). The 48-h and 12-h LC_{50}'s for the protozoan *Vorticella convallaria* var. *similis* were 0.075 and 0.29 mg Zn^{2+}/L, respectively (Sartory and Lloyd 1976). The 96-h EC_{50} (estimated concentration of toxicant that would stop any visible motion of the rotifers after the specified period of time when exposed to bright light) for the rotifer *Philodina acuticornis* was 1.2 and 1.5 mg Zn/L as $ZnSO_4$ and $ZnCl_2$, respectively, in soft water (25 mg/L total hardness) (Buikema *et al.* 1974). The toxicity of zinc to three zooplankters was tested by Baudouin and Scoppa (1974). The 48-h LC_{50}'s for *Cyclops abyssorum*, *Eudiaptomus padanus* and *Daphnia hyalina* were 5.5, 0.5 and 0.04 mg/L, respectively (water hardness 23 mg/L as $CaCO_3$). *Daphnia magna* was used as the test animal to study the effect of zinc on growth, reproduction and survival. The 48-h LC_{50} was 0.1 mg/L without food and 0.28 mg/L with food (suspension of powdered dried grass and enriched trout-fry granules) (total hardness 45.3 mg/L as $CaCO_3$). There was a 16% reproductive impairment after exposure for 3 weeks to 0.07 mg Zn/L. There was a 28% loss in weight after a 3-week exposure to 0.175 mg/L and 10% gain in protein per animal compared with the controls (Biesinger and Christensen 1972). The gain in protein probably reflected the changes in protein metabolism caused by an excess of zinc above that required for normal cellular functions.

Algae

Patrick *et al.* (1968) estimated the 120-h LC_{50} of zinc for the diatom *Nitzschia linearis*, regarded as being equivalent to the 96-h LC_{50} for bluegill, to be 4.3 mg/L (hardness of 100 mg/L as $CaCO_3$).

Effects of Other Heavy Metals on Zinc Toxicity

Hale (1977) showed that bioassays using water from a creek polluted by drainage from gold and silver mines and containing 0.018 mg Zn/L (range of <0.004 to 0.048 mg/L), <0.03 mg Cu/L, <0.002 mg Cd/L and other metals, indicated a 96-h LC_{50} of 0.55 mg Zn/L for rainbow trout (alkalinity, 105 mg/L). The full results (not quoted here) indicated that the toxicities of the various metals were additive and thus the direct application of results from controlled laboratory experiments to the field situation must be done with caution where the presence of other metals is known or suspected.

The concentration of zinc having an algicidal effect on *Selenastrum capricornutum* in the laboratory was 0.7 mg/L. The initial inhibition of growth began at 0.03 mg/L, and complete growth inhibition was caused by 0.12 mg/L. In the field, *S. capricornutum* was unable to tolerate zinc concentrations greater than 0.5 mg/L. The toxicity of zinc with copper – two metals which frequently occur together – on the growth of *S. capricornutum* indicated that the toxicities of zinc and copper were additive, thus lower concentrations of zinc in the presence of copper in the natural environment would be more toxic than expected. The combinations of 0.05 mg Zn/L plus 0.01, 0.02 and 0.03 mg Cu/L had the same effect as 0.06, 0.07 and 0.08 mg Zn/L, respectively (Bartlett *et al.* 1974).

The addition of sublethal combinations of copper and zinc decreased the heterotrophic activity of microflora from a natural pool. The inhibitive action of the metals was additive. The copper and zinc concentrations used in the study were 0.01 mg Cu/L and 0.05 mg Zn/L (Albright and Wilson 1974).

The growth rates of *Salvinia natans*, a floating fern, and *Lemna valdiviana*, a duckweed, were both stimulated by 0.05 and 0.08 mg Zn/L, respectively, when they were grown alone, but when *Lemna* was in competition with *Salvinia*, the stimulation of *Lemna* by zinc was less. The uptake of zinc by *Lemna* in the presence of *Salvinia* was greater than when *Lemna* was grown alone. Growth was much less and zinc uptake was greater in *Lemna* when both cadmium and zinc were present, indicating a synergistic action between the two metals. The toxicity of cadmium to *Lemna* and *Salvinia* was accentuated by the presence of zinc (Hutchinson and Czyrska 1975).

The effect of other metals on zinc toxicity should always be considered and effects on aquatic flora have already been discussed. Brown and Dalton (1970) showed that the toxicities of zinc, copper, nickel and phenol were additive to rainbow trout and therefore only fractions of the individual 48-h LC_{50} were necessary to cause the same deaths if the toxicants were presented as a mixture. The 48-h LC_{50}'s of copper, zinc and nickel were 0.75, 4.0 and 32 mg/L, respectively, in water with a hardness of 240 mg/L as $CaCO_3$. A mixture composed of 0.27, 1.33 and 10.67 mg/L copper, zinc and nickel, respectively, corresponded to the predicted 48-h LC_{50}. The toxicity of phenol was also additive when in combination with zinc and copper; the 48-h LC_{50} was caused by 0.25 mg Cu/L, 1.32 mg Zn/L and 3.13 mg C_6H_5OH/L. The 48-h LC_{50} for phenol alone was 9.4 mg/L. Marking (1977) also found that copper, zinc and nickel were additive in their toxicity to rainbow trout. Eaton (1973) studied a mixture of three metals: cadmium, copper and zinc. The chronic toxicity of the mixture was very similar to that of the zinc alone on fathead minnows (water hardness of 200 mg/L as $CaCO_3$).

Zinc and copper were synergistic and increased the lethal potency of the metals to mature guppies (*Poecilia reticulata*) by a factor of 2.5 above the predicted toxicity on the assumption of strict additivity of the metals' individual toxicities in water with a hardness of 124 mg/L as $CaCO_3$ (Anderson and Weber 1976). The hardness of the water appeared to govern whether copper and zinc were synergistic or additive in their action. Hard water (240 to 320 mg/L as $CaCO_3$) appeared to cause additive action (Lloyd 1961; Brown and Dalton 1970). Experiments using softer water, 15 to 124 mg/L as $CaCO_3$, have shown synergism (Lloyd 1961; Sprague 1964). When formulating water quality objectives for waters where copper and zinc are known to be present and a possible hazard, the effect of water hardness on mixtures should be studied carefully to determine whether addition or synergism would occur.

Spehar *et al.* (1978) exposed flagfish to mixtures of cadmium and zinc after studying the effects of the individual metals (0.008 mg Cd with 0.127 mg Zn/L; 0.006 mg Cd with 0.105 mg Zn/L; 0.004 mg Cd with 0.073 mg Zn/L). Survival of the larvae was not significantly different from the controls. Sexual maturity was not delayed, but mean spawnings per female and embryo production were lower than for the controls. No significant differences were observed in hatchability or larval growth and survival. It was concluded using this study and the single metal component study (see page 28) that the chronic toxicity of the mixtures of cadmium and zinc was little, if any, greater than the toxicity of zinc alone at the concentrations tested. Larvae initially exposed as embryos to the mixture were more tolerant than those not previously exposed in the egg stage. The acclimation observed was probably due to zinc, since similar results were not observed in a test with cadmium. Survival of larvae exposed as embryos was significantly decreased in both individual zinc and cadmium concentrations but not in mixtures of the metals, and this suggested that the metals acted antagonistically at this phase of the life cycle. Interpretation of the results is complex, as significant effects on survival were not observed in fish exposed to the same individual metal concentrations in the first-generation tests. Further study is needed.

Biesinger *et al.* (1978) have shown that mixtures of cadmium and zinc, and zinc and mercury caused significant decreases in the reproductive success of *Daphnia magna* at concentrations that had no effect as individual metals in chronic tests.

Exposure of the rotifer *Philodina acuticornis* to a mixture of zinc and copper indicated that there was basi-

cally no interaction between the two metals, though there is some difference of opinion among a number of authors (Buikema *et al.* 1977). The action of combinations of metals is not simple; different organisms may respond in different ways and there is still much research to be done.

Effects of Chemicals Other Than Heavy Metals on Zinc Toxicity

Aquatic organisms are not exposed to one toxicant alone nor are toxicants always presented at the same instant in real life situations. The chronic exposure of aquatic organisms to zinc reduced the survival time on subsequent exposure to acute concentrations of a second toxicant. Cairns *et al.* (1976) exposed snails (*Goniobasis livescens*) to 0.2 and 0.4 of the 48-h LC_{50} for zinc (1.54 and 3.08 mg Zn/L, respectively) and studied the time to death on exposure to an acute concentration of p-nitrophenol of 1000 mg/L. There were significant reductions in the survival times compared with the controls not previously exposed to zinc.

Pre-exposure of the snails to TFM (lampricide - 3-trifluoromethyl-4-nitrophenol) at concentrations of 2.3 and 4.6 mg/L or 0.2 and 0.4 of the 48-h LC_{50}, respectively, and subsequent exposure to zinc (500 mg/L) significantly reduced the survival time for the snails pre-exposed to 4.6 mg TFM/L, but not for those pre-exposed to the lower concentration of TFM (Cairns *et al.* 1976).

Metals also interact with pesticides, but very little has been found in the literature on such interactions. Roales and Perlmutter (1974) reported antagonism between zinc and Cygon, an organophosphorous pesticide, (*o*, *o*-dimethyl-*S*-(*N*-methylcarbamoylmethyl)-phosphorodithioate) in their toxicity to zebra fish embryos when the zinc was present in the mixture as 20% of the 72-h LC_{50} of 19 mg Zn/L and Cygon was present as 80% of the 72-h LC_{50} of 259 mg/L; 1.2% of the test fish were killed. Cygon alone at 80% of the 72-h LC_{50} (207 mg/L) caused a mortality of 30% and Speranza *et al.* (1977) reported a low embryo survival (0.9%) on exposure to 5 mg Zn/L, a level slightly higher than the 20% of the zinc 72-h LC_{50} (3.8 mg/L) used by Roales and Perlmutter. Higher mortalities (40% to 78%) were caused when the percentage of zinc and Cygon in the mixture were nearly equal or when zinc was present as 80% of the mixture.

The action between zinc and fluoride was antagonistic and the percentage of survival was greater than would have been expected when considering the action of the toxicant alone. The formation of metal complexes was suggested to explain these results (Buikema *et al.* 1977).

The toxicities of zinc and chlorine were less than strictly additive when zinc was present at concentrations of 60% or less in the mixture. At higher concentrations of zinc, e.g., 80%, the mixture was more additive in its toxic effect on the rotifer *Philodina acuticornis*. It was suggested that complexes were formed between zinc and chlorine when the concentration of chlorine was high (Buikema *et al.* 1977).

Chronic exposure to ammonia, another common pollutant, has been shown to increase the sensitivity of rainbow trout to acute poisoning by zinc from the 48-h LC_{50} of 2.45 to 1.8 mg Zn/L in water of hardness 290 mg/L as $CaCO_3$ (Water Research Centre 1967).

A rise in the phosphate content of water decreased the toxicity of zinc to a zinc-tolerant population of *Stigeoclonium tenue* (alga) but had little effect on a zinc-sensitive population (Harding and Whitton 1977). An increase in phosphate concentration decreased the toxicity of zinc to *Chlorella vulgaris* and *Plectonema boryanum* (Rana and Kumar 1974).

Chiaudani and Vighi (1978) studied the effects of low concentrations of zinc on the growth of the green alga *Selenastrum capricornutum* in culture media and in lake waters of different chelating capacities. The EC_{50} (the effective concentration which reduced the population growth to 50% of the control growth level) was studied using a normal culture medium containing EDTA (0.3 mg/L) and a modified medium with EDTA absent. The 96-h EC_{50} in normal medium was 0.027 mg Zn/L and 0.0044 mg Zn/L for modified medium. This agreed with the results of Bartlett *et al.* (1974), who used the same culture medium. Zinc toxicity varied in the different lake waters. For example, in water samples with a chelating capacity of 0.155 mg Cu/L, the presence of 0.02 mg Zn/L (approximately the culture 96-h EC_{50}) decreased the growth of *Selenastrum* to 77% of the control growth. In lake water with a lower chelating capacity (0.029 mg Cu/L) zinc was more toxic and growth was reduced to 42% of the control growth.

The chelator EDTA decreased the toxicity of zinc to the blue-green alga *Microcystis aeruginosa*. The strain used in the experiments did not have the gelatinous matrix, possessed by most wild strains of the genus, which could provide natural chelators that modify the effects of heavy metals in the environment. The green alga *Selenastrum capricornutum* and the diatom *Navicula seminulum* were much less sensitive than *Microcystis* at the same levels of zinc tested (Hall 1974). The possibility of the presence of synthetic chelators in the water as well as natural ones

will have to be considered when setting water quality objectives for specific bodies of water.

The presence of nitrilotriacetic acid (NTA) and EDTA has been shown to decrease the toxicity of zinc and copper. A series of 10-day bioassays with brook trout showed that the acute lethal levels were 0.75 mg Zn/L alone and 0.05 mg Cu/L alone. The toxicity of zinc-copper mixtures was additive. Most fish lived when the ratio of NTA to metal, in mg/L, was 2.0, and all lived when the ratios were 3.0 and 5.0, e.g., 0.1 mg Cu/L, 1.0 mg Zn/L and 2.2 and 3.3 mg NTA/L, respectively. The NTA was effective against the metals when they were alone or in mixtures. One molecule of NTA was accepted as chelating one ion of metal, and in the mixture, the copper was chelated first and the zinc afterwards. The same amount of zinc without NTA would have killed the trout in hours instead of days (water hardness 14 mg/L as $CaCO_3$). About 6 times as much EDTA as metal was required to prevent mortality (Sprague 1968b; Sprague *et al.* 1968). The relative non-toxicity of zinc-NTA chelates was also demonstrated using *Daphnia magna* in soft water (45 mg/L as $CaCO_3$). In the presence of Na_3NTA at a concentration of 2 mg/L, the calculated adult 3-week LC_{50} was 0.48 mg/L, while the LC_{50} for zinc alone was only 0.158 mg/L (Biesinger *et al.* 1974).

Humic acids were shown to have no appreciable effect on the acute toxicity of zinc to young Atlantic salmon in soft water (14 mg/L as $CaCO_3$) (Carson and Carson 1972). It has been suggested that high levels of calcium antagonize the chelation of zinc by humic acid, but Zitko (quoted in Cook and Cote 1972) reported that zinc is not readily chelated by humic acids.

Some ions were shown to affect the rate of uptake of zinc by the alga *Scenedesmus obliquus* when it was grown in the presence of zinc-contaminated clays. As the pH decreased, the clay selectively adsorbed H^+ and zinc was made available for absorption by *Scenedesmus*. Ferrous ions had no effect on the uptake of zinc by the algal cells, but phosphate appeared to affect the uptake of zinc. When clay was present, phosphate was preferentially adsorbed by the clay, therefore, more zinc was available in solution and was taken up by *Scenedesmus*. Copper and magnesium ions did not affect the adsorption of zinc by clay, but they interfered with the uptake of zinc by *Scenedesmus*. There was no competition between Zn^{2+} and Ca^{2+} for uptake by clay, but the uptake of zinc by *Scenedesmus* was stimulated by low concentrations of calcium ions, which played a role in the retention of zinc in the *Scenedesmus* cells. At high Ca^{2+} concentrations, less zinc was taken up by the algal cells and there was evidence of competition between the zinc and calcium for uptake (Keulder 1977). This work gives some indication of the roles played by suspended sediments and ionic composition of the water on the toxicity of zinc.

Studies found in the literature concentrated on using Zn^{2+} to investigate the toxicity of zinc, but colloidal forms have been found to be toxic (P.A. Spear, National Research Council of Canada Associate Committee on Scientific Criteria for Environmental Quality, personal communication). Further investigation into this aspect of zinc toxicity would give more understanding of the subject.

Sublethal Effects of Zinc on Fish

Reproduction

Fathead minnow spawning and hatching success and fry survival during exposure to zinc was studied by Brungs (1969) in water of hardness 200 mg/L as $CaCO_3$, using a range of zinc concentrations from 0.18 to 3.8 mg Zn/L. Egg production was shown to be the most sensitive stage. Eggs were rarely spawned in 1.3, 0.66 and 0.32 mg Zn/L, although typical spawning behaviour was exhibited. A zinc concentration of 0.18 mg/L caused an 83% reduction in the number of eggs, but hatching and fry survival at 0.66, 0.32 and 0.18 mg/L were similar to that of the controls. Eggs incubated at 1.3 mg Zn/L hatched successfully, but there was gradual mortality of the fry and survival was 30% and 49% at 20 days. The MATC lay between 0.18 mg/L, the lowest unacceptable concentration, and 0.03 mg/L (controls).

The toxicity of zinc in soft water (46 mg/L as $CaCO_3$) to fathead minnows (*Pimephales promelas*) was investigated by Benoit and Holcombe (1978). The most sensitive stage was just after spawning during water hardening. Egg adhesiveness and fragility were significantly affected at 0.145 mg Zn/L but not by 0.078 mg Zn/L. The hatchability and 8-week survival were significantly reduced and deformities were significantly increased by 0.295 mg/L. Growth was not affected by any of the concentrations tested, 0.045 to 0.295 mg Zn/L. Fish transferred from 0.295 mg Zn/L, where they had produced abnormal eggs, to water with no added zinc, produced normal eggs within a few days after transfer. The 96-h LC_{50} for the minnows was 0.6 mg/L and the MATC based on egg adhesiveness and fragility was between 0.078 and 0.145 mg Zn/L.

Sublethal studies on the survival and growth of flagfish (*Jordanella floridae*) (Spehar 1976) indicated a maximum acceptable toxicant concentration (MATC) between 0.026 and 0.051 mg Zn/L; the 96-h LC_{50} was 1.5 mg/L. Flagfish have been shown to be similar to rainbow trout in sensitivity to zinc in water of hardness 45 mg/L as $CaCO_3$. The survival of fish larvae not previously exposed to zinc as

embryos was adversely affected by 0.085 mg Zn/L, and growth of adult females exposed to 0.051 mg Zn/L was significantly lower than that of the controls. Both concentrations were lower than that affecting reproduction, as the mean spawnings per female and embryo production at 0.085 mg Zn/L were lower than but not significantly different from the controls. This contrasted with the work by Brungs (1969), who found that reproduction was the most sensitive measure of zinc toxicity. Larvae previously exposed to zinc as embryos were more tolerant than those not previously exposed (Spehar 1976).

Further studies were conducted which exposed flagfish to sublethal levels of zinc (0.073 to 0.139 mg/L) for one complete life cycle in soft water of 45 mg/L as $CaCO_3$. Testing was begun at the embryo stage. The survival of larvae not exposed as embryos was significantly reduced at all zinc exposures, but the survival of larvae exposed to zinc as embryos was only affected significantly by 0.139 mg Zn/L. Most of the zinc was found in the chorion of the eggs (70%), so the embryo was only exposed to a fraction of the zinc in solution and became acclimatized to the metal. Sexual maturity of the fish was delayed, normal spawning behaviour was decreased at all exposure levels and the fish were hyperactive during feeding or just before spawning (Spehar *et al.* 1978). The fish were also exposed to mixtures of zinc and cadmium, and these results were discussed in the section on "Toxicity to fish eggs."

Three generations of brook trout (*Salvelinus fontinalis*) were exposed to zinc concentrations ranging from 0.002 to 0.534 mg/L and no significant harmful effects were apparent. Egg fragility and embryo survival were significantly reduced by 1.36 mg Zn/L in water of hardness 45 mg/L as $CaCO_3$. The 96-h LC_{50} was 2.0 mg/L. Slight growth enhancement was observed in second-generation trout after 73 weeks of exposure at 0.266 and 0.534 mg Zn/L (Holcombe *et al.* 1979).

The MATC for rainbow trout in water of hardness 30 mg/L as $CaCO_3$ was between 0.14 and 0.26 mg/L for fry hatching from eggs which had been exposed to zinc. The MATC for fry hatching from unexposed eggs was between 0.036 and 0.071 mg/L, indicating acclimation (Goettl *et al.* 1976?). The latter MATC was similar to that for flagfish (Spehar 1976). The MATC was much higher in hard water (350 mg/L as $CaCO_3$) and lay between 0.32 and 0.64 mg Zn/L for fish hatching from unexposed eggs (Goettl *et al.* 1976?).

A study of 21 months investigated the chronic effects of zinc on sockeye salmon (*Oncorhynchus nerka*) and consisted of a 3-month exposure of adults followed by an 18-month exposure of the embryonic through smolt stages. Adults were exposed to concentrations of 0.03 to 0.112 mg Zn/L and there were no apparent adverse effects. The embryos and young stages were exposed to an additional 0.24 mg/L, and survival, growth and osmoregulation on subsequent transfer to seawater were not adversely affected by these concentrations. A significant acclimation to zinc occurred in the 1 month old alevins exposed to zinc as shown by the fact that 72% of the control alevins died when they were exposed to 0.63 mg Zn/L (115-h LC_{50} 0.447 mg/L), but all of the zinc pre-exposed (0.24 mg/L) alevins survived. Acclimation was also demonstrated using acute toxicity tests on 9 month old parr. Spawning behaviour could not be observed in this study, as the fish were spawned manually; the authors also questioned whether the 3-month exposure of adults to zinc was long enough to affect fecundity. The water quality varied during the 21 months of the test, and there were periods of elevated alkalinity (range 18 to 61 mg/L as $CaCO_3$) and hardness (range 18 to 91 mg/L as $CaCO_3$), which may have changed the toxicity of zinc during those periods. There were no apparent effects on the fish from an increase in temperature during the period of high temperature (14.5°C) that occurred during the first few weeks of egg incubation. Dissolved oxygen levels fell below 6.0 mg/L on five occasions during the 6-month post-hatch period (minimum 4.2 mg/L) but caused no mortality (Chapman 1978).

The reproduction and growth of bluegills (*Lepomis macrochirus*) did not appear to be affected by 0.035 and 0.076 mg Zn/L in water of hardness 51 mg/L as $CaCO_3$, but 0.235 mg Zn/L inhibited spawning in ripe bluegills and killed newly hatched fry (Sparks *et al.* 1972). The 96-h LC_{50} in soft water (20 mg/L as $CaCO_3$) was 0.485 to 0.582 mg/L (Pickering and Henderson 1966). The growth of rainbow trout in very hard water (374 mg/L as $CaCO_3$) was unaffected by 0.214 and 0.52 mg Zn/L, but was significantly decreased by 1.12 mg/L over an 85-day exposure period (Watson and McKeown 1976). The growth of yearling minnow (*Phoxinus phoxinus*) was more sensitive than the growth of adults when exposed to zinc in soft water over a 150-day period. Yearling growth was reduced by 0.13 and adult growth by 0.2 mg Zn/L (Bengtsson 1974b). A number of authors have remarked on the excitable state and paralysis of fish during exposure to zinc; this could have an effect on their survival (Bengtsson 1974a; Lorz and McPherson 1976).

Respiration

Hughes and Adeney (1977) studied the effects of zinc (40 and 10 mg/L) on cardiac and ventilatory rhythms of rainbow trout (*Salmo gairdneri* Richardson). The higher of the two concentrations increased the ventilatory and cough frequency and decreased the heart rate, reactions which are

similar to those occurring in environmental hypoxia (low oxygen). Exposure to 10 mg/L did not cause significant effects, but it was noticed that when zinc-exposed fish were held in water with reduced dissolved oxygen concentrations, the ability of the fish to respond to the lack of oxygen in the water had been affected by the zinc. Other studies also report on the effect of zinc on ventilatory rate and coughing (Sparks *et al.* 1971; Cairns *et al.* 1973).

The effect of zinc on oxygen consumption has been documented by a number of authors. The zinc inhibition of oxygen uptake by mitochondria was studied by Hiltibran (1971). Tissue hypoxia as a result of exposure to zinc affecting gaseous exchange at the gills was supported by the work of Burton *et al.* (1972a). The reduction by zinc of oxygen uptake at the gill, because of gill damage, was demonstrated by Burton *et al.* (1972a), Matthiessen and Brafield (1973) and Skidmore (1970). Damage to the gill epithelium was the probable cause of decreased oxygen uptake and not the copious production of mucus (Lloyd 1960).

Skidmore (1970) used acutely lethal concentrations of zinc to try to determine the physiological cause of death. Gill ventilation volume increased 6-fold, oxygen utilization decreased 7-fold, the heart rate was halved, the coughing rate increased 18-fold, and the P_{O_2} (partial pressure of oxygen in mm Hg) of the dorsal aortic blood declined. The osmotic pressure of the blood and the concentration of major cations (Na, K, Ca, Mg) and zinc were largely unaffected during the experimental period. Histological examination (Skidmore and Tovell 1972) indicated that the initial changes in the gill tissue were typical of an acute inflammatory reaction and included the lifting of the epithelium of the gill lamellae and a collapse of the tissues partially or completely occluding the central blood spaces. Intracellular changes were present. The presence of large numbers of granulocytes indicated that the blood was stagnated.

Effect of Zinc on Swimming Ability

The capability of fish to adapt to the effects of zinc was also illustrated by behavioural studies. The swimming capabilities, i.e. the ability to compensate for torque in a rotating water current, of the minnow *Phoxinus phoxinus* was affected by exposure to zinc. The younger fish were more sensitive and a significant effect on the ability of under yearlings to compensate for torque was caused by 0.06 mg Zn/L after exposure to zinc for 108 days. Significant effects were noted for yearlings at 0.16 mg/L and for adults at 0.2 mg/L. The author stated that none of the parameters - mortality, growth, reproduction or histology - gave evidence of toxic effects at 0.06 mg Zn/L over the period tested. Even though the test is not directly applicable to the field situation, changes in swimming capabilities will be of consequence to the survival of fish (Bengtsson 1974c).

Parasitism and Disease-causing Organisms

Fish in the wild state are often infected by parasites and this could lower their resistance to other stresses. The susceptibility of juvenile sockeye salmon (*Oncorhynchus nerka*) to zinc was increased by infections of the intestinal parasite *Eubothrium salvelini* (Cestoda). A study by Boyce and Yamada (1977) demonstrated that there was a significant increase in susceptibility to zinc in fish carrying the intestinal parasite.

Snails (*Lymnaea stagnalis*) parasitized by trematodes were tested for their susceptibility to zinc. There was a definite reduction in the tolerance to acutely lethal concentrations of zinc in snails carrying parasites; the reduction was less evident in snails that had been newly parasitized (Guth *et al.* 1977).

Zinc appeared to suppress the immune response of the zebra fish against the bacterium *Proteus vulgaris* but not against the infectious pancreatic necrosis virus. This factor is one which must be considered where waters carry important fisheries (Sarot and Perlmutter 1976).

Avoidance of Zinc by Fish and Insects

Rainbow trout avoided solutions of zinc sulphate, the threshold avoidance level* being 0.0056 mg/L of added zinc. The actual concentration avoided was 0.0086 mg/L, as the background level of zinc in the water was 0.003 mg/L. This was, coincidentally, close to 0.01 of the lethal threshold concentration of zinc. There did not appear to be any effect on the avoidance threshold owing to temperature when the trout were tested at 9.5°C and 17°C. These temperatures are well within the natural water temperature range of the trout. Increasing the background level of zinc in the water during acclimation or testing from 0.003 to 0.013 mg/L did not appear to have a significant effect on the threshold avoidance level of 0.0056 mg/L of added zinc. The total hardness of the water was between 13 and 15 mg/L as $CaCO_3$ (Sprague 1968a). The level of zinc which was detected by the fish was below that having an adverse effect on the life cycle, but these low levels would

* Threshold avoidance level = the concentration of zinc which caused a response in 50% of the presentations of zinc to the fish in the test apparatus, in which they were given a choice between water with or without the added zinc.

be of importance during periods of migration, as a fish might be prevented from reaching spawning areas.

The avoidance of copper-zinc mixtures by young Atlantic salmon was at 0.02 of the incipient lethal level (ILL: a sharp boundary between lethal and non-lethal concentrations) of equally toxic amounts of the two metals (ILL for copper, 0.048 mg/L; zinc, 0.6 mg/L; hardness, 20 mg/L as $CaCO_3$). Under field situations, a higher threshold for avoidance would be present owing to territorial or migrational motivation, which give fish a strong drive to remain or to travel in a river. A significant downstream movement by fish that had recently gone upstream occurred when the copper and zinc levels were above 0.35 to 0.43 ILL during 4 years of observation (Sprague *et al.* 1965).

Studies with chironomid larvae indicated that sediments contaminated with heavy metals were avoided and there was a positive linear relationship between the amount of zinc in the sediment and the level of avoidance. A very hard water was used: 340 mg/L as $CaCO_3$. Most of the zinc in the sediment was in the carbonate form and less than 1% was exchangeable. The threshold of avoidance seemed to be at zinc concentrations between 4385 and 8330 mg/kg. The exact amount of zinc available to the midge larvae was not known. The study indicated the possibility of avoidance of heavy metal contamination by the more mobile macroinvertebrates (Wentsel *et al.* 1977c).

Recommended Objective for Aquatic Life Inhabiting Inland Waters

The lowest 96-h LC_{50} values for fish in soft water were between 0.296 and 0.5 mg Zn/L, and in hard water, 2.5 mg Zn/L. Some of the microcrustaceans were more sensitive, for example, the 48-h LC_{50} for *Daphnia hyalina* was 0.04 mg/L and for *Daphnia magna* 0.1 mg/L without food and 0.28 mg/L with food.

The maximum acceptable toxicant concentrations in soft water for rainbow trout lay between 0.036 and 0.071 mg Zn/L, for flagfish between 0.026 and 0.051 mg/L, and for bluegill between 0.076 and 0.0235 mg/L using survival and growth of fish larvae. In some other species, egg production was the most sensitive stage, but to slightly higher levels of zinc. A 16% reproductive impairment in *Daphnia magna* occurred after a 3-week exposure to 0.07 mg/L. Growth inhibition in algae began at 0.03 mg Zn/L.

Maximum acceptable toxicant concentrations for fathead minnow, flagfish and rainbow trout were plotted against hardness, and on a first approximation, a linear relationship seems to exist between MATC and hardness. The available data, however, are not sufficient to allow the derivation of an exact equation. Consequently, the following levels of zinc are recommended as objectives, using the classification of hardness given in the *Hydrological Atlas of Canada* (1978) as a guide.

Hardness, mg/L as $CaCO_3$	Zinc, mg/L as total zinc
0 - 120	0.05
120 - 180	0.10
180 - 300	0.20
>300	0.30

A maximum zinc concentration of 0.05 mg/L is recommended for the protection of aquatic life in soft and medium surface waters with a hardness of <120 mg/L as $CaCO_3$. This level is above the concentration of zinc that can be detected by salmonids, and in soft waters where migration occurs, for example by Atlantic salmon, the recommended level may have to be lowered.

The International Joint Commission (IJC 1976) recommended level for the Great Lakes is 0.03 mg Zn/L, as is that of the European Inland Fisheries Advisory Commission (EIFAC) for European fish in water with a hardness of 10.0 mg/L as $CaCO_3$. For waters with hardness >10.0 mg/L as $CaCO_3$, EIFAC recommended 0.2-0.5 mg Zn/L (EIFAC 1973).

The presence of other metals could accentuate the toxicity of zinc, and environmental factors such as temperature, dissolved oxygen and pH could be exerting additional stress. The recommended levels should provide an adequate safety margin in the field, as most of the detrimental effects were observed under laboratory conditions.

The acclimation to zinc, when present, increases the safety margin. Lakes in the Flin Flon area of Manitoba held apparently viable populations of fish with approximately 0.01 mg Cu/L and 0.09 mg Zn/L, a zinc concentration which, under laboratory conditions, had an adverse effect on fish.

It is considered that at this time, there is insufficient knowledge available to be able to recommend different levels of zinc for different alkalinities and pH, as has been done with water hardness.

The natural levels of zinc in some areas of Canada are above the recommended objectives. In these cases the natural level is recommended as the objective.

Wildlife

Insufficient information was found in the literature on which to recommend a limit for zinc in natural waters. Muskrats living in an area where high levels of heavy metals were found in aquatic vegetation (4887.9 mg Zn/kg, dry weight) contained elevated levels in the liver (81.2 mg Zn/kg) and bone (305 mg Zn/kg) (fresh weight) compared with those animals living in areas not heavily contaminated by heavy metals (plants 60, liver 33.4 and bone 97.7 mg Zn/kg). Mammals and other aquatic organisms utilizing aquatic habitats accumulate zinc from the environment. The levels of zinc in the muskrats did not seem to produce any detrimental effects (Everett and Anthony 1976).

The limit recommended for aquatic life should give adequate protection for wildlife.

Water Supply for Livestock

Essentiality of Zinc in Animal Nutrition

Zinc forms an essential element in the diet of farm animals such as poultry, swine, cattle and sheep by participating in their protein and carbohydrate metabolism. Zinc deficiency leads to retardation of growth, disorders of bones and joints, skin diseases and low fertility (Farnsworth and Kline 1973). Dietary zinc deficiency is also accompanied by a reduction in the plasma zinc concentration and plasma alkaline phosphatase activity, and an increase in the ^{65}Zn uptake *in vitro* by cells of whole blood (Chesters and Will 1978; Kirchgessner *et al.* 1977). The zinc uptake *in vitro* by the cells in the whole blood was 3 to 5 times faster for non-ruminants than for ruminants (Chesters and Will 1978). These last symptoms also appear in animals with low food intake, reduced dietary protein content and endotoxin administration. This is why it is sometimes difficult to diagnose zinc deficiency in an animal.

Iniguez *et al.* (1978) reported malformations in chick embryo blastoderm owing to zinc deficiency; the younger the blastoderm, the greater was its sensitivity to zinc deficiency.

Wethers fed on a diet containing 5 mg Zn/kg, as $ZnSO_4 \cdot H_2O$, developed signs of zinc deficiency. Animals fed on a diet containing the same level of zinc but in a sequestered or chelated form did not develop these signs, although the zinc status, in terms of plasma zinc and plasma alkaline phosphatase activity, was lower than in the animals on a zinc-sufficient diet (Ho and Hidiroglou 1977).

Administration of zinc, as $ZnSO_4$ aqueous solution, to sheep by intraruminal intubation on three to four occasions over a period of 24 to 30 days at a rate of 100 or 200 mg Zn/kg body weight resulted in reduced feed intake, increased secretion of acid from the abomasum and increased duodenal pH (McLeay and Smith 1977).

To provide an adequate zinc intake, levels of 40 to 65 mg/kg have been suggested for zinc concentrations in various chicken feeds and levels of 20 to 30 mg/kg in duck feeds (Muller *et al.* 1976). Underwood (1971) quoted 35 mg Zn/kg of diet as being the minimum zinc requirement for poultry. The same author also gave values for other farm animals. Thus, for pigs the estimated requirement was around 40 mg Zn/kg of diet if clinical symptoms of parakeratosis were to be avoided, and around 100 mg/kg for adequate growth. High dietary intakes of calcium and copper raised these requirements. For ruminants (sheep, cattle) the minimum zinc requirement was estimated at approximately 35 mg/kg of diet. Sauchelli (1969) quoted a value of 50 mg Zn/kg of feed as being sufficient to assure normal growth of animals.

A significant difference, 0.49 vs. 0.86 mg/L, was found in the zinc plasma concentrations of 5-week-old Holstein calves receiving 18 and 518 mg/kg dietary zinc, respectively. When the diet contained 68 mg Zn/kg, the difference was not significant (Kincaid 1978).

The addition of zinc-methionine to the basal diet of broiler chicks resulted in improved weight gain and feed utilization (Sanford 1976).

In a trial experiment, zinc, as $ZnSO_4 \cdot 7H_2O$, in concentrations of up to 225 mg/L, was administered to cattle for the control of sporidesmin, a facial eczema toxin. The toxin was controlled, and a faster weight gain was noticed than in the control group (Wright *et al.* 1978).

Toxicity of Zinc to Animals

Diets containing levels of zinc in the range of 16.7 to 628.3 mg/kg did not cause any significant differences in the growth rate, efficiency of feed conversion, or the levels of zinc in the hair or serum of growing beef cattle (Beeson *et al.* 1977).

Leeper (1978, p. 13) quoted a value of 1000 mg Zn/kg of diet as being possibly harmful to animals. The same value, 1000 mg/kg, was estimated as being the maximum safe dietary zinc concentration for pigs. Higher concentrations, i.e., 2000 mg/kg (as $ZnCO_3$), reduced feed intake and growth, and caused arthritis and gastritis (Neathery and Miller 1977b). At zinc concentrations of 4000 and 8000 mg/kg the mortality was high (Underwood 1971). Dietary levels of 500 mg/kg had no effect on steers; concentrations of 900 mg/kg reduced weight gains and lowered

food efficiency (Underwood 1971). Similarly, levels of 600 mg Zn/kg of diet did not lead to any differences in the zinc concentrations in various tissues of mature non-lactating cows when compared with controls. However, when the same diet was administered to young dairy calves the zinc concentrations in the kidney, liver and pancreas increased several fold (Neathery and Miller 1977a); thus it has been estimated that the safe dietary concentration of zinc is approximately 500 mg/kg for growing cattle and 1000 mg/kg for mature animals. Higher than normal zinc concentrations were found in the sperm and the seminal plasma from Jersey bulls with the "Dag defect," a hereditary and sterilizing condition in which sperm tails are coiled, folded or split into fibres (Blom and Wolstrup 1976).

Lambs maintained on a diet with yeast as the protein source and zinc content of 840 mg Zn/kg showed a low appetite and poor growth rates. Postmortem examination revealed kidney lesions and zinc concentrations in the cortex ranging from 2720 to 7943 mg/kg (dry weight). The zinc concentration in the kidney cortex of lambs on a normal diet ranged between 299 and 320 mg/kg (Davies *et al.* 1977). Dietary levels of 750 mg Zn/kg and 2.5 mg Cu/kg caused abortions, decreased survival, and lowered copper concentrations in the plasma and liver of pregnant ewes (Neathery and Miller 1977a). It has been concluded that with adequate dietary levels of Cu, Fe and Ca the maximum safe dietary zinc concentration for sheep is approximately 600 mg/kg.

For poultry, concentrations greater than 1500 mg Zn/kg (as carbonate or sulphate) reduced the growth and the feed efficiency. Concentrations of 2000 mg Zn/kg were tolerated by chicks without adverse effects when marginal amounts of vitamin D were added to the feed (Neathery and Miller 1977b). Feed intake, body weight and egg production of White Leghorn hens were reduced at zinc dietary levels of 794, 1585 and 2512 mg/kg (as zinc acetate) (Hermayer *et al.* 1977). A very high level of dietary zinc, 10 000 mg/kg of diet (as zinc oxide or acetate), resulted in complete cessation of egg production in laying hens. The egg production resumed 11 or 12 days after the high zinc intake was stopped (Shippee *et al.* 1977). Similar results were reported by Scott and Creger (1976). The addition of only 250 mg Zn/kg of feed slightly depressed the egg production of laying hens but improved the shell thickness of eggs (Sanford 1977). Adverse effects on turkey were observed only at concentrations of 4000 mg/kg. The safe dietary levels of zinc were estimated at 1000 mg/kg for chicks and 2000 mg/kg for turkeys (Neathery and Miller 1977b).

The Interaction of Zinc with Other Metals in Animal Nutrition

Dietary zinc supplementation, 420 mg Zn/kg of diet, prevented the development of copper toxicosis in sheep. The liver damage and the copper concentration in the liver were reduced. A slight anemia developed in animals receiving this high zinc diet (Bremner *et al.* 1976).

Zinc-supplemented diets at a level of approximately 100 mg/kg reduced the copper and cadmium concentration in the livers of various farm animals, e.g., lambs, sheep, calves. Elevated diet concentrations of cadmium, and to a lesser extent copper, increased the zinc concentration in the liver (Mills 1974).

Zinc concentrations in various hen's tissues ranged from 125 (muscles) to 244 mg/kg (femur). The eggs contained 60 mg Zn/kg. Administration of 200 mg Cd/kg of diet significantly decreased the zinc concentrations in muscles, femur and feathers; increased the zinc concentration in the liver; and left the kidney and egg concentrations unchanged. In goat dams fed on a normal diet the zinc concentrations in the kidney and liver were 87 and 158 mg/kg, whereas the concentrations in the kids were 101 and 239 mg/kg, respectively. The zinc concentrations in the kidney and liver of dams fed on a diet containing 75 mg Cd/kg until their death (the last of the animals died after 19 months) increased to 330 and 421 mg/kg, respectively. The kids from these dams had kidney and liver zinc concentrations of 86 and 94 mg/kg (Anke *et al.* 1970).

A diet containing 40 mg Zn/kg or more prevented the growth depression caused by 400 mg Ni/kg (as $NiCl_2$) in chicks. Zinc, however, did not have any effect on mercury or cobalt toxicity (Hill 1977).

Recommended Objective for Water Supply for Livestock

Data in the published literature show that dietary zinc levels of 50 to 100 mg/kg are necessary to prevent the development of zinc deficiency in farm animals. Zinc becomes toxic at levels of 500 to 1000 mg/kg of diet depending on the animal and its age.

In the United States, an upper limit of 25 mg Zn/L in water for livestock was recommended (NAS/NAE 1973, p. 317). In Australia, a level of 20 mg/L has been recommended (Hart 1974, p. 127).

Based on the data summarized here, it is recommended that the maximum zinc concentration in the water supplies of livestock should be 50 mg/L. This concentration

provides an adequate safety margin for zinc toxicosis while allowing for an adequate intake of zinc, an essential element in animal nutrition.

Water for Irrigation

Zinc Concentration in Soils and Plants

The concentration of zinc in soils has been variously estimated at 50 mg/kg (Brooks 1977), 10 to 20 mg/kg (Bolter *et al.* 1975), or 10 to 300 mg/kg (Lindsay 1972; Berry and Wallace 1974). Usually sandy soils have low zinc content, 10 to 30 mg/kg, since the zinc concentration in quartz is low.

Zinc, like other metals, is found in higher concentrations in the topsoil than in the subsoil, probably because of the higher percentage of organic matter in the former and, in certain circumstances, because of atmospheric deposition (Leeper 1978, p. 76ff.; Lagerwerff and Specht 1970). Near a lead smelter, zinc was heavily concentrated in the leaf litter and the top 0.6 cm of soil. For example, the concentration in the leaf litter was 330 mg/kg; in the top 0.6 cm of soil, 100 mg/kg; and then it dropped to 30 mg/kg below a depth of 2.5 cm (Bolter *et al.* 1975). In the Sudbury region of Northern Ontario the zinc concentrations in soil around the nickel and copper smelters varied over a narrow range of 50 to 100 mg/kg (mean 68 mg/kg) within a radius of 0.8 to 50 km, from the surface to a depth of approximately 12 cm (Costescu and Hutchinson 1972).

The range of zinc concentrations in agricultural soils of Ontario was 4.6 to 162 mg/kg with an average value of 53.5 mg/kg. Sandy soils had the lowest average, 39.9 mg/kg, while the highest average, 66.3 mg Zn/kg, occurred in organic soils. It was concluded that these were normal values and that neither agricultural nor industrial activities had increased them (Frank *et al.* 1976b). Another study showed that despite the use of some zinc compounds as pesticides on orchard and vineyard soils of Southern Ontario, the zinc concentration in these soils had not increased (Frank *et al.* 1976a).

The mean total zinc concentration in a number of soil samples from Southwestern Ontario ranged between 71 and 88 mg/kg; the overall range was 35 to 163 mg/kg. The mean DTPA (diethylenetriaminepentaacetic acid) extractable zinc concentration ranged from 0.22 to 1.70 mg/kg; the overall range was <0.04 to 6.71 mg/kg. This represented 0.3% to 1.9% of the corresponding total zinc concentration (26 soil samples analyzed for total zinc but only 19 samples analyzed for extractable zinc). The correlation coefficient r between the two zinc concentrations was +0.48. Good positive correlations with r's of 0.76 to 0.81 were found between the total zinc concentration and the clay, aluminum and iron contents of the soil. The correlation with the organic matter content of the soil was not very good (r = 0.38) (Whitby *et al.* 1978).

The zinc concentration in soil samples from Southern and Western Manitoba ranged between 24 and 350 mg/kg with an average of 91 mg/kg. No significant difference was found between the zinc content of rural and urban (Winnipeg) soils (Mills and Zwarich 1975).

The average 1 *N* HCl extractable zinc content of various soils (well or poorly drained; brown, black or gray soil zone) in Alberta ranged from 5.7 for well-drained brown soils to 26 mg/kg for poorly drained gray soils. Wheat and barley seeds from these soils contained 22 and 62 mg Zn/kg. The straw contained 4.9 to 24 mg Zn/kg (Dudas and Pawluk 1977).

The average total zinc concentration in surface agricultural soils in the interior of British Columbia was 105 mg/kg (John 1975). Application every second year, for 13 years, of a sludge containing 4890 mg Zn/kg (dry weight) at a rate of approximately 2500 mg Zn/kg of soil per year (i.e. 6.4 t/ha.a) to a soil containing 97.9 milligrams of acid-extractable zinc per kilogram (dry weight) raised the extractable zinc concentration to 368.9 mg/kg. (It can be calculated that approximately 33 000 mg Zn/kg of soil were added during the 13-year period.) The zinc concentration in the vegetation rose from 34.3 mg/kg to 114.5 mg/kg (dry weight) (Andersson and Nilsson 1972).

The zinc content of various crops ranged from approximately 0.7 mg/kg in tomatoes (fresh weight) to about 214 mg/kg in cottonseed and lint. Grains and hay, with zinc concentrations of 11 to 71 mg/kg, occupy an intermediate position (McCalla *et al.* 1977). On a dry weight basis, the average zinc concentration in some vegetables ranged from 33.9 mg/kg (potatoes) to 235.1 mg/kg (parsley). The corresponding mean total zinc concentration of the soil was 526.9 mg/kg, but the mean extractable zinc concentration varied depending on the extracting agent. It ranged between 27.7 mg/kg (extracting agent, 1 *N* NH_4OAc, pH 7.0) and 401.0 mg/kg (1.0 *N* HCl) (Låg and Elsokkary 1978).

The average zinc concentration in a series of vegetables grown in British Columbia ranged from 11 mg/kg (dry weight) in potato to 110 mg/kg (dry weight) in spinach. The overall range was 3 to 435 mg/kg. The zinc concentration in soil averaged 81 to 205 mg/kg. In any particular vegetable, the zinc concentration varied by a factor of up to 20, depending on the location (Warren *et al.* 1970).

Hinesley *et al.* (1978) have shown with corn that in addition to high levels of available zinc for plant uptake in soils, the capacity of certain plants to accumulate zinc might be under genetic control. In general young seedlings have higher zinc concentrations than more mature plants. Usually roots have higher zinc content than the tops, especially if the concentration of available zinc in the growing medium is high (Lindsay 1972; Wallace and Romney 1977). In zinc-deficient situations, the zinc is translocated from the roots to the tops. The zinc content of plant parts decreases in the order roots, stem, leaves, fruit (Sauchelli 1969).

Some plant species, e.g. *Aspergillus microcysticus* Sappe (mold) and *Sphagnum acutifolium* Ehrh. (moss), contained well over 500 mg Zn/kg (dry weight) (Horovitz *et al.* 1974).

Earthworms, a key component in the natural food chain and an important organism in soil mixing and in maintaining physical soil characteristics and processes (aeration, water permeability, mineral turnover), accumulate zinc. In some east Tennessee soils the concentration factors ranged from 3 to 13. The soil zinc concentrations ranged from 30 to 57 mg/kg and the earthworm zinc concentrations from 93 to 502 mg/kg (dry weight) (Van Hook 1974).

Availability of Zinc from Soils to Plants

The transfer of zinc from soil or irrigation water to plants is a complex phenomenon and its rate depends on a variety of factors such as soil characteristics (composition, pH, cation exchange capacity, etc.), the plant, the chemical form of the metal, the type and frequency of irrigation, the volume of irrigation water (Delmas *et al.* 1978).

Effluents from columns packed with a variety of soils with pH's of 4.2 to 7.8 and zinc concentrations from 40 to 320 mg/kg, and leached with deionized water, had zinc concentrations ranging from "below the detection limit" to 0.5 mg/L. When the leachate was H_2SO_4 of pH 3.0, the zinc concentration in the effluent ranged from "below the detection limit" to 1.3 mg/L. The highest zinc and other metals concentrations in the effluent were obtained with a solution of (0.025 mol $AlCl_3$ + 0.025 mol $FeCl_2$)/L at pH 3.0. In this case the zinc concentration ranged from 0.1 to 13 mg/L (Fuller *et al.* 1976).

Aqueous extraction of a liquid (1.46% solids) sludge containing 872 mg Zn/kg (dry weight) released 4.38% of the zinc, and 2.79% was released by aqueous extraction of a 'dry' (53.5% solids) sludge sample containing 13 723 mg Zn/kg (dry weight) (Sidle and Kardos 1977a).

Irrigation with chlorinated secondary treated wastewater effluent containing 0.197 mg Zn/L for a period of 7 years did not increase the 0.1 *N* HCl extractable zinc concentration in the soil. Irrigation for a further period of three years with a mixture of effluent and liquid sludge containing 0.73 mg/kg increased the soil concentration in the top 30 cm from approximately 2.9 to 7.4 mg/L. Below this depth the concentration was not affected. During the entire 10-year period an estimated 72.2 kg Zn/ha or approximately 29 mg Zn/kg was applied to the soil of which about half was applied during the first seven years. Similarly, only a very small increase from 1.67 (control plot) to 3.13 mg/kg was observed in the 0.1 *N* HCl - extractable zinc concentration, in the soil of a corn-growing area irrigated with treated wastewater effluent for 11 years. During this period the total amount of zinc applied was 31 kg/ha or approximately 12 mg Zn/kg of soil. When only half of this amount was applied, the resulting soil concentration was only 2.11 mg Zn/kg (Sidle *et al.* 1977).

In a series of experiments, among the various compounds used to "extract" zinc in soil analyses, DTPA (diethylenetriaminepentaacetic acid) seemed to give the best correlations with the zinc content of plants (Lindsay 1972; MacLean 1974; Keeney and Walsh 1975). In another set of experiments several reagents such as 1.0 *N* HCl, 0.1 *N* HNO_3, 1.0 *N* NH_4OAc at pH 4.8, 2.5% (v/v) acetic acid, ammonium lactate at pH 3.75, ammonium oxalate at pH 3.25 and 0.5 mol EDTA/L all gave very high positive correlations (correlation coefficients of 0.67 to 0.99) between the "extractable" zinc concentration of soil and the zinc content of plants (potatoes, carrots, cabbage, barley, etc.). At the same time correlation coefficients of 0.84 to 0.99 were obtained between the various "extractable" zinc concentrations and total zinc content of soil (Låg and Elsokkary 1976). A much poorer correlation, i.e. a correlation coefficient of 0.48, between DTPA-extractable zinc and total zinc concentration was obtained by Whitby *et al.* (1978). This shows that the extractability of zinc with DTPA depends very much on the characteristics of each individual soil. For example, DTPA-extractable zinc increased with increasing organic matter content and decreased with the increasing clay content of the soils (Webber and Corneau 1975). Korcak *et al.* (1979) also obtained poor correlations between DTPA-extractable zinc and other metals (Cu, Ni, Cd) in soil and the concentration of the same metal in the leaves of the pearl millet, red oak and black walnut trees. Data also showed that extractable (DTPA) zinc concentration in soil decreased with time after application of sewage sludge to the land. Similarly, the zinc concentration in plant tissues decreased with successive crops. This probably shows that with time zinc converts to less available forms (Kelling *et al.* 1977; Korcak *et al.* 1979).

Experimental results have shown that DTPA, EDTA and fulvic acid can chelate the zinc from soils and that the ratio of the concentration of the zinc chelate to that of the free Zn^{2+} in soil solutions at pH's >7 increases with increasing pH. Thus ligands can be effective in maintaining zinc in a soluble form in alkaline soils (Sinha *et al.* 1977). Results quoted by Lindsay (1972) show also that approximately 60% of the zinc present in soil is complexed and that good positive correlations were found between soluble zinc and soluble organic matter concentrations, and between extractable zinc and organic matter concentrations in soils. The fulvic and amino acids complexes, for example, have high water solubilities, whereas the humic acids form insoluble metal complexes. High concentrations of the soluble fractions are likely to be found near decomposing plant residues, as they are formed and destroyed by soil microorganisms in a continuous process. The breakdown of organic zinc chelates is one reason for the increase in the zinc ion concentration (Lagerwerff 1967). Bunzl *et al.* (1976) determined, in batch experiments, the rates of adsorption and desorption of zinc and other metals by soil organic matter in the form of an aqueous suspension of HCl-washed peat. The half-times of adsorption for zinc, i.e., the time at which half of the equilibrium uptake is attained, ranged from around 8 s (at an initial concentration of ~3.3 mg Zn^{2+}/L) to 30 s (at an initial concentration of ~0.33 mg Zn^{2+}/L). The half-times of desorption ranged from about 7 to 12 s, depending on the initial concentration of the zinc on the peat and the hydrogen ion concentration.

The pH of the soil is another very important factor in determining the amount of soluble zinc in soils. An empirical relation reported by Lindsay (1972) showed that zinc ion concentration was directly proportional to the squared hydrogen ion concentration, for example, one unit increase in pH led to 100-fold decrease in the Zn^{2+} concentration. Jenne (1968) quoted data showing that zinc availability reached a minimum at pH 7.5 and that zinc toxicity caused by overfertilization was inhibited at pH 6 and above. Experiments conducted by James and MacNaughton (1977) showed also the strong dependence on pH of adsorption of zinc ions from solution onto minerals such as cinnabar, manganese oxide, silica oxide or aluminum oxide.

When zinc and other metals were applied to soils, it was estimated that 90% or more was retained in the soil, 1% was removed by leaching, and 0.1% to 10% was removed with the crop products (Andersson and Nilsson 1972). In experiments conducted by Kelling *et al.* (1977) plants removed 1% to 3% of the zinc added to the soil (less than 1% of other metals - Cu, Cd, Ni and Cr - was removed by crops). Similarly, the first crop of barley removed only 2.5% of the zinc added to the soil through the application of sludge (Dowdy and Larson 1975a). The zinc uptake by barley plants increased linearly with increased rates of sludge application. The same linearity was observed for snap beans until a certain maximum was reached. The zinc levels did not increase further with additional sludge applications nor did they decrease once sludge applications ceased (Dowdy *et al.* 1978). Almost 97% of the zinc was retained in the soil when an anaerobically digested sewage sludge was applied to plots in a mixed-hardwood forest. The application rate of zinc was 28.5 kg/ha or approximately 11 mg/kg. Tests have shown that the applied zinc was only slightly more extractable with 0.1 *N* HCl than the zinc already present in the soil (Sidle 1977; Sidle and Kardos 1977b).

The zinc content of lettuce increased from 47 to 350 mg/kg (dry weight) when the soil was treated with sewage from two western Canadian cities at a rate of approximately 32 mg Zn/kg. The zinc in sewage displayed a relatively high solubility (Dudas and Pawluk 1975). Lettuce is a very good metal accumulator; carrots and potatoes are non-accumulators (Dowdy and Larson 1975b). For example, when approximately 200 mg Zn/kg of soil was added (as sewage sludge), the zinc concentration in lettuce increased from 21 to 225 mg/kg. With the same amount of zinc added, the concentration in the potatoes increased from 24 (controls) to 53 mg/kg.

Jennett and Linnemann (1977) found that soils tested in a series of experiments had the ability to sorb levels of zinc and lead ranging from 20.7% to 90.3% of the cation exchange capacity (CEC) depending on the soil and solution characteristics. Once sorbed, the metals could not be removed by rainwater, but they could be partially removed by strong chelating agents, e.g. humic acids. The zinc concentrations in leachates from sites in the United States receiving residential and commercial wastes ranged from 0.07 to 33.0 mg/L (James 1977). It has been recommended that for agricultural soils the total toxic element load that a given soil receives should not exceed 5% of the soil CEC at pH > 6.5 (Garrigan 1977).

Chelating agents are sometimes added to fertilizers to increase the concentration of zinc in soil solution. The Zn-EDTA complex has a maximum stability at pH 6.5, where 70% of the ligand was chelated to zinc. At low pH, Fe^{3+}, and at high pH, Ca^{2+} displace zinc from this complex. Similarly, Zn-DTPA complex reaches maximum stability at pH 7.3 (Lindsay 1972). In nutrient solutions at pH's greater than 6, chelating agents decrease the Zn^{2+} concentration, leading eventually to zinc deficiency. Zinc uptake by plants is also depressed by alkaline earth metals, the order of effectiveness being $Mg^{2+} > Ca^{2+} = Ba^{2+} = Sr^{2+}$ (Lindsay 1972). Experimental results suggest, however, that at least

with corn Zn^{2+} is the form of zinc which is absorbed by plant roots and that chelation only aids in the transport of metal to plant roots. It was calculated that a concentration of 10^{-10} mol/L free zinc ions in solution (approximately 2 ng/L) was sufficient to prevent zinc deficiency in corn grown in nutrient solutions (Halvorson and Lindsay 1977).

Sinha and Prasad (1977) reported a significant linear relationship between the concentration of soluble zinc in soil and its uptake by wheat. A good positive correlation was found between the 0.1 *N* HCl-extractable zinc in soil and the zinc content of corn leaves grown in it (Freedman 1977). A very strong positive correlation was found between the zinc adsorbed by some alkaline soils and their clay, organic carbon and $CaCO_3$ contents, and CEC (cation exchange capacity). Strong positive correlations were also found between the same soil characteristics and the amount of zinc retained by the soil after sequential desorption with 1 mol KCl/L and 0.05 mol $Cu(CH_3COO)_2$/L. The retaining capabilities of clay and of organic matter were due mainly to their CEC. No correlations were found between the adsorption of zinc from solution by soils or retention of zinc by the same soils and their pH's (Singh and Sekhon 1977). The intensity of zinc adsorption increases with increasing fineness of soil texture. In coarse-textured soils the weakly adsorbed or electrostatically bonded zinc is high and hence more mobile than in fine-textured soils (Sidhu *et al.* 1977a, b). Sauchelli (1969) quoted data which showed that the adsorption of zinc by soil increased up to pH 6.5 and then it remained constant.

Good negative correlations were found between the sum of zinc and copper concentrations in the organic topsoil from coniferous forests surrounding a brass mill in southeastern Sweden and the decomposition rate of organic matter, the phosphorus and nitrogen mineralization rates, and the activities of soil urease and acid phosphatase (Tyler 1975).

The yield of rye and corn increased slightly or did not change from the controls when various combinations of refuse and sludge were applied to the soil. The application rate for zinc was between 30 and 120 mg/kg of soil. The zinc levels in plant tissues increased, especially in the case of corn stover and ear leaf but not as much in the corn grain (King *et al.* 1974).

Cabbage grown on anaerobically digested municipal sewage sludge contained 224 mg Zn/kg (dry weight), whereas the zinc concentration in the control plants was 17 mg/kg. The sludge itself had a zinc concentration of 1418 mg/kg (dry weight) (Bisht *et al.* 1976).

The yield of soybean seeds was not affected by the addition of approximately 40 mg Zn/kg of soil, but the concentration of zinc in leaves and seeds increased (Ham and Dowdy 1978). The zinc concentration of sorghum and soybeans grown in soils treated with sewage sludge known to have high concentrations of zinc (11 800 mg/kg) and other heavy metals was higher than that of the grains grown in control soils. The zinc concentration in sorghum and soybean grains from the control soils was 14.2 and 49.0 mg/kg, respectively. The zinc concentration in the same grains grown in the soils treated with sewage sludge ranged from 20.4 to 22.1 mg/kg in sorghum, and from 63.2 to 68.6 mg/kg in soybeans. Corn grain from the control and from the sewage sludge-treated soils had the same zinc concentrations (Miller and Boswell 1976). No difference was found in the zinc concentration of liver and kidney tissues of weanling rats fed the grains grown in the control and sewage sludge-treated soils (Miller and Boswell 1976).

In another case, although the concentration of DTPA-extractable zinc of soil increased with the application of a sewage sludge from approximately 2.5 mg/kg to up to approximately 120 mg/kg (at application rates of up to approximately 400 mg total Zn/kg of soil), no increased zinc content (with the exception of pearl millet, which showed an increase 3 months after the application of the sewage sludge compost) nor visual or foliar effects were noted in the growth of pearl millet or tree seedlings of red oak and black walnut (Korcak *et al.* 1979).

In still another experiment, zinc, in a digested sewage sludge, was applied for 5 years at an annual average rate of 258 kg/ha or approximately 100 mg/kg to a plot of silt loam soil cultivated with corn. The total zinc concentration in this soil reached 451 mg/kg after the last year of application and then dropped to around 320 mg/kg in the subsequent 3 years. During the entire period the zinc concentration in the control plots remained fairly constant between 72 and 84 mg/kg. The concentration in the grain ranged between 38 and 45 mg/kg (dry weight) during the application and then decreased to 27 mg/kg 4 years after the sludge application had stopped. The grain from the control plot contained between 16 and 25 mg Zn/kg (Hinesley *et al.* 1979).

Essentiality of Zinc to Plants

In plants, zinc is an essential component of several enzymes such as carbonic anhydrase, alcohol dehydrogenase and glutamic dehydrogenase. Zinc catalyzes oxidation processes in plant cells, participates in the formation of growth-promoting compounds and in the transformation of carbohydrates, and provides the absorption of water. Zinc-deficient plants are low in indoleacetic acid (IAA, the main natural hormone in plants), water and tryptophane, a precursor of IAA (Lindsay 1972; Farnsworth and Kline 1973).

Some crops, e.g., fruit trees (particularly citrus, peaches, apples, and pecan), pineapple, corn, beans and onions, are sensitive to zinc deficiency in soil. Grasses, legumes and small grain crops are rather insensitive to zinc deficiency. Small leaves with rosette-type terminal growth and interveinal chlorosis are among the visual symptoms of zinc deficiency. Zinc deficiency can occur in sandy soils where the total zinc content is low; in high rainfall areas, where acidic conditions prevail as a result of leaching; in alkaline (calcareous) soils of pH >7.4 where zinc availability is decreased; and in places where the topsoil has been removed and exposed subsoil has a much lower organic content and a higher pH. Low soil temperatures during the early growing season can also lead to zinc deficiency. High levels of applied or available soil phosphorus have also been implicated in zinc deficiency by interfering with the uptake, translocation or utilization of zinc. Nitrogen fertilization can increase the severity of zinc deficiency (Chapman 1966; Lindsay 1972).

Zinc deficiency seems to occur at various "extractable" soil concentrations depending, among other things, on the extraction method used in the analysis and the plant type. For example, acute zinc deficiency in pineapple occurred at extractable (ammonium acetate at pH 4.6) zinc concentrations of 0.5 to 0.6 mg/kg. At concentrations of 1.7 to 3.5 mg/kg no zinc deficiency occurred. Zinc deficiency was observed in wheat and barley at "extractable" (0.1 *N* $MgSO_4$) zinc concentrations of 3.5 to 6.6 mg/kg. The maximum yields were obtained at concentrations of 40 mg/kg (rye), 95 mg/kg (barley), 160 mg/kg (wheat) and 480 mg/kg (oats) (Chapman 1966). Other data quoted in the same paper show that zinc deficiency occurred at "extractable" (0.1 *N* HCl) zinc concentrations of 0.5 to 1.3 mg/kg and that no deficiency was observed at values of 1.20 to 4.70 mg/kg. The pH values of the soil ranged from 4.7 to 6.2.

In a greenhouse experiment the addition of 5 to 15 mg Zn/kg of soil (as $ZnSO_4$) increased the dry-matter yield of wheat. This increase was accompanied by an increase in the zinc uptake by the plants and in the zinc concentration in the straw and grains (Chahal and Randhawa 1977).

The yield of radishes increased by 50% to 60% when the "extractable" (1 *N* HCl) zinc content of soil increased from 10.1 to 59.8 mg/kg. A corresponding increase was observed in the plant zinc content. In the soil with low zinc content the concentration of the roots ranged from 40.0 to 80.7 mg/kg (dry weight). The range in the soil with high zinc content was 59.6 to 121 mg/kg (Lagerwerff 1971).

Zinc Toxicity to Plants

Zinc excess leads to iron chlorosis in certain plants such as citrus fruit trees, oats and sugar beets (Chapman 1966). A negative correlation between the root iron and the leaf zinc content of corn plants was reported. Similarly, the root zinc content was negatively correlated with the leaf iron content. Both soil and corn leaf zinc contents were negatively correlated with the chlorophyll content (Freedman 1977). Chapman (1966) quoted data showing that chlorosis occurred in sugar beet plants grown in sand when the nutrient solution contained approximately 30 to 65 mg Zn/L. Oat plants began to show signs of iron chlorosis at a culture solution concentration of 25 mg Zn/L. The leaves contained 1700 mg Zn/kg (dry weight). At zinc concentrations of 100 mg/L the chlorosis was severe and the leaves contained 7500 mg Zn/kg (Hunter and Vergnano 1953). A nutrient solution containing 65 mg Zn/kg caused a mild chlorosis of young expanding leaves and a decrease in both the fresh and dry matter yields of barley. The range of zinc concentration in the stem and leaves rose from 4.6 to 14.0 mg/kg (dry weight) in the controls and to 558 to 600 mg/kg in the plants grown in the nutrient solution containing the excess zinc. In the roots the zinc concentration went up from 203 mg/kg, in the controls, to 2650 mg/kg. Excess zinc also decreased the iron concentration in roots. The activity of ribonuclease was significantly stimulated by the same zinc concentration (65 mg/L) (Agarwala *et al.* 1977). Also in barley it was reported that the critical levels of zinc in the culture solutions ranged from 3.5 to 12.6 mg/L and the corresponding tissue concentrations ranged from 124 to 220 mg/kg (dry weight). The "critical level" was defined as being the concentration of the element, in solution or in the tissue, at which yield is first reduced by the toxic effects of the element. In other words, the dry matter yield is independent of the metal concentration in the photosynthesizing tissues of the plants up to a critical concentration characteristic for each metal. The yield then decreases as some function of the metal concentration. In a different growing condition the tissue critical levels for young (fire-leaf) spring barley varied between 168 and 518 mg Zn/kg (dry weight), the median being 210 mg/kg. The corresponding nutrient solution concentrations ranged from 78 to 96 mg Zn/L. For ryegrass the critical tissue and solution concentrations were 221 mg Zn/kg and 2.8 mg Zn/L, respectively (Beckett and Davis 1977; Davis and Beckett 1978).

Other visual signs of zinc toxicity are reduced size of leaves, necrosis of leaf tips and shoot apices, a reddish tint near the basal part of leaves, curling and distortion of foliage (Bisht *et al.* 1976). Flax grown in nutrient solutions

containing 2.5 mg Zn/L or more (as $ZnSO_4 \cdot 7H_2O$) showed signs of iron deficiency (Millikan 1947). Lindsay (1972) quoted results which showed that plants exhibited toxic effects at zinc concentrations in nutrient solutions in the range of approximately 0.065 to 0.4 mg/L. The maximum growth was obtained at concentration levels of approximately 0.016 mg/L. Pratt (1973) quoted a zinc concentration of 0.4 mg/L as being fatal to the Peking variety of soybeans.

The yield reduction for chard leaves started at an added zinc concentration in soil of 65.4 mg/kg at a soil pH of 5.3 or 6.4. The corresponding tissue concentrations were 1058 and 337 mg/kg (dry weight), respectively. At pH 7.2 the critical soil concentration was 262 mg Zn/kg and the corresponding tissue concentration, 406 mg/kg (Chaney 1973).

Leeper (1978, p. 52ff.) quoted data which showed that a concentration of 585 mg Zn/kg of soil was toxic to Swiss chard and spinach. The zinc concentration in the chard reached 800 mg/kg.

The maximum yield with corn grown in hydroponic solutions was obtained at zinc and iron concentrations of 0.1 and 1.4 mg/L, respectively. Increasing the zinc concentration to 0.6 mg/L led to chlorosis and reduced the root and shoot weights by approximately 50%. A normal growth was obtained when the iron concentration was raised to 50 mg/L. Significant positive correlations were found between the zinc concentration in the nutrient solution and the zinc content of the roots and leaves. Significant negative correlations were found between the iron concentration in the nutrient solution and the zinc content of roots and leaves (Rosen *et al.* 1977).

An excess of zinc, 65 mg/L, reduced the yield of barley grown in a sand culture by 44% compared with controls. The activity of some enzymes, e.g., B-glycerophosphatase and aldolase, was also reduced by approximately 30%. The activity of ribonuclease, however, increased by 41% (Bisht *et al.* 1976).

Zinc-enriched nutrient solutions produced phytotoxicity, interveinal chlorosis, stunted growth, wilting of the new growth and finally necrosis of the leaf and stem tissue in 2- and 3-year-old seedlings of red maple (*Acer rubrum* L.), white pine (*Pinus strobus* L.) and Norway spruce (*Picea abies* L.) grown under greenhouse conditions. The root growth was positively correlated with the zinc concentration in the nutrient solution and started to be reduced at a zinc concentration of approximately 0.100 mg/L (0.050 mg/L for red maple). The leaves started to accumulate zinc at concentrations of 0.025 mg Zn/L. The same symptoms of zinc toxicity were observed when the seedlings were grown in zinc-amended soils. Early zinc toxicity was observed at zinc concentrations in soil of 41.2 mg/kg (white pine), 82.5 mg/kg (red maple) and 165.1 mg/kg (Norway spruce) (Mitchell and Fratz 1977).

Zinc was also found to be toxic to wheat and lettuce, although less so than Cd, Cu or Ni. The accumulation of zinc, however, in the aerial tissues of these plants was greater than that of other metals (Mitchell *et al.* 1978). Wheat yield was significantly reduced at added zinc concentrations to the soil of more than 500 mg/kg at pH 5.5. At higher pH's (6.5 and 7.5) no such reduction was observed (Webber 1972).

The threshold for acute zinc toxicity on lettuce seedlings in culture solution, as measured by the reduction in the root length, was 4 mg/L; complete growth inhibition occurred at 46 mg/L (Berry 1977).

In pot experiments the lettuce yield decreased abruptly starting with added zinc concentrations of 120 mg/kg (Rideau clay, no lime, pH 5.3) and 240 mg/kg (Grenville loam, pH 6.3). This reduction was accompanied by a large increase in the zinc concentration in the plant itself. While in the controls the zinc concentration ranged from 75 to 87 mg/kg, at the two treatment levels mentioned above the zinc concentration increased to 417 and 259 mg/kg, respectively. The yield was further reduced and the zinc concentration in the plant increased when more zinc was added to the soil. The yield stayed approximately the same as in the controls and the zinc concentration in the plant tissue increased slowly with the added zinc when the clay soil was limed to pH 6.5 (MacLean and Dekker 1978). The amount of zinc extracted by 0.005 mol DTPA/L and by 0.01 mol $CaCl_2$/L increased as the amount of zinc added to the soils increased. The lettuce yield was reduced by 25% when zinc was added to an acidic soil (pH 5.7) at a rate of 130 mg/kg. The addition of 580 mg Zn/kg of soil reduced the wheat yield by the same percentage. The addition of 160 mg Zn/kg to an acidic soil resulted in a zinc concentration in the lettuce leaf of 1058 mg/kg (dry weight). The accumulation of zinc was always greater in acidic (pH 5.7) than in calcareous (pH 7.5) soils by a factor ranging from approximately 1 to 5. The zinc availability, as measured by the DTPA-TEA (Diethylenetriaminepentaacetic acid - Triethanolamine) or saturation extracts, was greater in acidic than in calcareous soils. Excellent positive correlations were obtained between the zinc concentration in wheat and lettuce leaves and the zinc concentration in soils measured by the DTPA-TEA or saturation extract methods. In contrast, however, the phytotoxic yield reductions were observed at much lower zinc tissue concentrations in plants grown in calcareous soils than in plants grown in acidic soils (Mitchell *et al.* 1978).

Garrigan (1977) calculated that the maximum allowable zinc load on "surface soils" is approximately 560 kg/ha or 220 mg/kg of soil.

The Interaction between Zinc and Other Compounds in Plants

The zinc concentrations in spinach and barley increased by up to 44% as a result of NaCl applications to the soil in amounts of up to 2250 mg/kg of soil; the percentage increase in cadmium concentration in the two plants was even greater. The concentration of zinc in the saturation extract of the soil was also increased with the application of NaCl. The highest increase was at the highest levels of applied Zn and NaCl. This increase in the zinc solution concentration was attributed to the displacement of zinc from the available binding sites by sodium and to the formation of zinc complexes with the chloride ion (Monette 1978).

The concentration of cadmium in spinach was reduced with the application of 20 mg Zn/kg of soil (Monette 1978). The zinc uptake tended to increase when beetroot, lettuce, radish and tomato were grown in nutrient solutions containing 0.01 or 0.1 mg Cd/L, levels which did not affect yields. The reverse, i.e., a reduction in the zinc uptake, was noticed for carrots and Swiss chard (Turner 1973).

Some phosphate fertilizers contain zinc, and concentrations as high as 2400 mg Zn/kg have been reported (Lagerwerff 1967; Williams 1977). Application of fertilizers containing 285 to 715 mg Zn/kg (Idaho and North Carolina phosphate rock) in amounts of 200 and 600 mg P/kg (pot experiments) increased the total zinc uptake by corn per pot. However, when the zinc uptake was expressed as milligrams of zinc per kilogram of plant (dry weight), the uptake decreased. In the control pots the zinc uptake ranged between 39 and 101 mg Zn/kg of plant (dry weight), while the range in the pots to which fertilizer was added was 20 to 29 mg Zn/kg of plant (dry weight). This decrease was due to the large increase, 200% to 700%, in the corn production as a result of the fertilizer application (Mortvedt and Giordano 1977). It is interesting to note that the 0.1 *N* HCl-extractable zinc concentrations in soil, after the removal of the corn crop, in the control pots and the pots to which fertilizer had been added were approximately the same. The uptake of zinc by corn decreased by more than half when the pH of the soil was raised from 5.7 to 7.8. Phosphorus fertilizer showed a tendency to decrease zinc (also Cu, but not Ni) in the lettuce and to increase the extractable zinc (and Ni) in the soil (MacLean and Dekker 1978).

In a pot experiment, an added zinc concentration of 250 mg/kg to a soil already containing 53 mg Zn/kg and having a pH of 4.9 reduced the corn yield slightly, the alfalfa yield markedly and prevented the growth of lettuce. These effects were not observed in soils of pH 6.8 to 7.5. The zinc content of plants increased with the addition of zinc to the soil, reaching the highest values - 792 mg/kg in corn and 702 mg/kg in alfalfa - in the soil of pH 4.9. Pretreatment of the soil with 500 mg P/kg, as $CaH_4(PO_4)_2 \cdot H_2O$, increased the yields of corn and lettuce but not of alfalfa. It did not eliminate, however, the toxic effects of zinc in the acidic soil in the case of lettuce and alfalfa, although the yield reduction of the alfalfa was not as great as with no phosphorus treatment. The phosphorus treatment also increased the levels of zinc extractable with DTPA, $MgCl_2$ or $CaCl_2$. This did not result, however, in an increased zinc concentration in the plant tissues (MacLean 1974).

The addition of nickel to the soil decreased slightly the zinc concentration in lettuce from that found in the control and it was accompanied by a yield decrease (MacLean and Dekker 1978).

Molybdenum at levels of 5 mg/L or higher counteracted the iron deficiency produced in flax grown in nutrient solutions containing 2.5 mg Zn/L or more (Chapman 1966).

There were reports that toxicity symptoms owing to zinc appeared to be alleviated by treating the soil with iron chelates, nutrient solutions with copper chelates, or by application of nitrogen or potassium fertilizers (Lagerwerff 1967).

Zinc decreased the uptake of boron by alfalfa, and the plants developed boron deficiency symptoms when boron and zinc were added to the soil together. Zinc seemed to interfere with the use or transport of boron to the top of the plant (Brown and Graham 1978).

Recommended Objective for Irrigation Waters

Zinc is both an essential and a toxic element to plants. The soil concentrations at which zinc becomes toxic vary greatly with the nature and the characteristics of the soil and the plant itself. There are results in the published literature showing that some toxic effects start to appear at zinc concentrations in soil of around 50 mg/kg of soil. For plants grown in nutrient solutions the toxic concentrations of zinc seemed to start around 0.4 mg/L, although some lower values have been reported.

The published literature on this subject also shows that 90% or more of the zinc reaching the soil is retained by it and that only a small percentage, 1% to 3% of the total zinc in soil, is taken up by plants.

Assuming an irrigation rate of 0.9 $m^3/m^2.a$ (or 3 acre-feet per acre per year) and adequate liming to keep the pH above 6, Pratt (1973, p. 27) recommended a zinc concentration of 2 mg/L in irrigation water for continuous use on all soils. On acid sandy soils the suggested maximum concentration was 1 mg/L. At this concentration approximately 8 mg Zn/kg of soil will be added every year through the irrigation water.

In the United States, NAS/NAE (1973, p. 345) have recommended a maximum zinc concentration in irrigation waters of 2 mg/L for continuous use on all soils at a pH above 6. For alkaline or neutral soils for a 20-year period a maximum concentration of 10 mg/L has been recommended. In Australia (Hart 1974, p. 111) a maximum concentration of 2 mg Zn/L has been recommended for irrigation water.

Based on the data summarized here, a maximum zinc concentration of 1 mg/L is recommended for irrigation waters in soils with a pH below 6.5. At pH's above this value a maximum concentration of 5 mg/L is recommended.

Recreation and Aesthetics

Potable water supplies in recreational areas should comply with the level of 5 mg/L total zinc for raw public water supplies. The level recommended for aquatic life, 0.05 to 0.30 mg Zn/L depending on water hardness, is much lower and will ensure the safety of any water used for contact sports.

Recommended Objective for Recreational Waters

The recommended objective for zinc in natural waters used for recreational purposes is 5 mg/L total zinc.

Industrial Water Supplies

The only industry in which the concentration of zinc in the process water is of importance is the food industry.

The general principle is that water which is incorporated in the final product should meet the same requirements as those for drinking water.

Recommended Objective for Industrial Water Supplies

An objective of 5 mg/L of total zinc, or 10 mg/L where the water will be treated before entering the distribution system, is recommended for water that is incorporated in the final product in the food industry. This includes the water used for cooling cans in the canning industry.

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